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in Ionic Liquids“

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Curriculum Vitae

Abstract

Niobium is widely used because of its many unique properties: superconductivity, thermal and mechanical stability, high corrosion resistance, physiological inertness, etc. The electrochemical deposition of niobium as well as of other refractory metals such as Ta, Ti, Zr, Mo, W can be achieved only from non-aqueous electrolytes because of their relatively negative deposition potentials. High temperature molten salts consisting of alkali metal halides with different salts of niobium were found to be the efficient baths for niobium electroplating. In general, a main disadvantage of such electrolytes is high operating temperatures (600-900°C) at which the substrate can suffer thermal damage and structural changes; the corrosion problems arise also at these temperatures. Therefore, the low-temperature molten salts, or ionic liquids are an attractive alternative media for electrochemical deposition of refractory metals at temperatures below 200°C. Ionic liquids give a chance for the development of the principle new energy saving and environmental friendly technologies and extension of the area of application of the coatings of refractory metals.

The series of the novel ionic liquids consisting of 1-butyl-1-methylpyrrolidinium chloride (Pyr₁₄Cl) as an organic part and different salts of niobium(V), namely NbCl₅ and K₂NbF₇ as an inorganic one were synthesized at various mole fractions of the components for the potential electrochemical application. The mixtures (x)Pyr₁₄Cl-(1-x)NbCl₅ form liquids in a wide range of compositions from x=0.85 up to x=0.20 at different temperatures (140-170°C). The mixtures (x)Pyr₁₄Cl-(1-x)K₂NbF₇ form liquids at ~170-180°C in basic-neutral range of compositions (x=0.80÷0.50); acidic ionic liquids (x=0.40÷0.20) are formed at ~190°C.

The Raman and FTIR spectroscopy was used to obtain the information about the complexes of niobium(V) formed during the mixing of the Pyr₁₄Cl with K₂NbF₇ or NbCl₅ and about the possible formation of the complexes of niobium in lower oxidation states. The structure and composition of niobium(V) species in the basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ and (x)Pyr₁₄Cl-(1-x)K₂NbF₇ (x=0.85-0.20) was investigated over the temperature range 20-200°C by means of *in situ* Raman spectroscopy. According to the Raman data, in basic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures at x=0.85-0.80, the self-reduction of niobium(V) to tetravalent state was observed. Octahedral species NbCl₆⁻ were identified in the range of compositions x=0.85-0.50. In acidic mixtures at x=0.45-0.20, the niobium(V) species are present in the form of Nb₂Cl₁₀ and Nb₂Cl₁₁⁻. The formation of octahedral, NbF₆⁻ and hepta-coordinated, NbF₇²⁻ species was confirmed in both acidic and

basic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇. These species exist in the equilibrium, NbF₆⁻ ↔ NbF₇²⁻, slightly affected by the composition of ionic liquids and temperature.

Electrochemical characterisation of niobium(V) in ionic liquids was performed using different techniques (cyclic voltammetry, chronoamperometry and chronopotentiometry) and various set of the electrodes with respect to the electrochemical deposition of niobium. The influence of the temperature, composition, presence of niobium powder or using niobium soluble electrode as well as the additives of alkali metal halides on the reduction of niobium(V) in ionic liquids for the sake of electrodeposition of niobium was investigated in details. The mechanism of electrochemical reduction of niobium(V) in ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ and (x)Pyr₁₄Cl-(1-x)K₂NbF₇ (x=0.85-0.20) was estimated on the base of electrochemical data in combination with the spectroscopic findings. Electroplating experiments were carried out in the most preferable ionic liquids using various techniques and substrates complemented by ESEM/EDAX investigations.

Kurzfassung

Niobium wird vor allem dank seinen einzigartigen Eigenschaften wie Supraleitung, thermische und mechanische Stabilität, hohe Korrosionsbeständigkeit, physiologische Trägheit etc. breit eingesetzt. Die elektrochemische Abscheidung von Nb ebenso wie Abscheidung anderer Refraktärmetallen wie Ta, Ti, Zr, Mo, W kann ausschließlich aus nichtwässrigen Elektrolyten aufgrund des relativ negativen Abscheidungspotenzials erreicht werden. Die hochtemperaturigen Salzschnmelzen, die aus Alkalimetall-Halogeniden mit diversen Niobiumsalzen bestehen, sind die effizientesten Medien für elektrochemische Abscheidung von Niobium. Im Allgemeinen bedeuten hohe Betriebstemperaturen (600-900°C), unter denen Substraten an thermischen Schädigungen und strukturellen Änderungen leiden können, was auch zu weiteren Korosionsproblemen führen kann, einen wesentlichen Nachteil solcher Elektrolyten. Deshalb stellen die niedrigtemperaturigen Salzschnmelzen bzw. Ionische Flüssigkeiten attraktive alternative Medien für elektrokemische Abscheidung von Refraktärmetallen bei Temperaturen unter 200°C dar. Die ionischen Flüssigkeiten geben der Entwicklung von neuen energiesparenden und umweltfreundlichen Techologien sowie der Erweiterung des Einsatzgebiets von Refraktärmetallenbeschichtungen eine Chance.

Es wurde eine Reihe von neuartigen ionischen Flüssigkeiten, die sowohl aus organischem Teil (1-butyl-1-methylpyrrolidinium chloride (Pyr_{14}Cl)) als auch aus anorganischem Teil (NbCl_5 und K_2NbF_7 Niobiumsalzen) bestehen, bei verschiedenen molaren Anteilen von Komponenten für elektrokemische Anwedungen synthetisiert. Die Mischungen $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ bilden Flüssigkeiten im weiten Bereich der Kompositionen von $x=0.85$ bis $x=0.20$ bei diversen Temperaturen (140-170°C). Die Mischungen $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ bilden Flüssigkeiten bei ~170-180°C in basischem und neutralem Bereich der Kompositionen ($x=0.80\div 0.50$); saure ionische Flüssigkeiten ($x=0.40\div 0.20$) bilden sich bei ~190°C.

Für Auswertung der Informationen über Niobium(V)-Komplexe, die infolge der Mischung von Pyr_{14}Cl mit K_2NbF_7 oder NbCl_5 erhalten wurden, sowie Informationen über mögliche Bildung von Niobiumkomplexen niedriger Oxidationsstufen, wurden Raman- und FTIR-Spektroskopie angewendet. Die Struktur und Zusammensetzung von Niobium(V)-Spezies in basischen und sauren ionischen Flüssigkeiten $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ und $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ ($x=0.85-0.20$) im Temperaturbereich 20-200°C wurden mittels *in situ* Raman-Spektroskopie untersucht. Laut Daten, die mit Hilfe von Raman-Spektroskopie bekommen wurden, wurde in basischen ionischen Flüssigkeiten $((x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ Mischungen $x=0.85-0.80$) Selbstreduktion von Niobium(V) in vierwertigen Zustand beobachtet. Im

Bereich der Kompositionen $x=0.85-0.50$ wurden oktaedrische Spezies NbCl_6^- identifiziert. In saueren Mischungen $x=0.45-0.20$ sind Niobium(V)-Spezies in Form von $\text{Nb}_2\text{Cl}_{10}$ und $\text{Nb}_2\text{Cl}_{11}^-$ vorhanden. Die Bildung von oktaedrischen NbF_6^- und heptakoordinierten NbF_7^{2-} Komplexen wurde sowohl in saueren als auch in basischen ionischen Flüssigkeiten $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ bestätigt. Diese Spezies befinden sich im Gleichgewicht $\text{NbF}_6^- \leftrightarrow \text{NbF}_7^{2-}$, welches von Komposition und Temperatur der ionischen Flüssigkeiten leicht beeinflusst wird.

Die elektrochemische Charakterisierung von Niobium(V) in ionischen Flüssigkeiten ist mit Hilfe von verschiedenen Techniken (die Cyclische Voltammetrie, Chronoamperometrie und Chronopotentiometrie) sowie verschiedenen Elektroden-Sätzen zwecks elektrochemischer Abscheidung von Niobium zustande gekommen. Es wurde Einfluß von Temperatur, Komposition sowie Vorhandensein von Niobiumpulver bzw. Verwendung von löslicher Niobiumelektrode neben den Zusätzen von Alkalimetall-Halogeniden auf die Reduktion von Niobium(V) in ionischen Flüssigkeiten zur Abscheidung von Niobium detailliert untersucht. Der Mechanismus elektrochemischer Reduktion von Niobium(V) in ionischen Flüssigkeiten $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ und $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ ($x=0.85-0.20$) wurde aufgrund der Kombination von elektrochemischen und spektroskopischen Daten festgestellt. Die Beschichtungsversuche wurden in am meisten geeigneten ionischen Flüssigkeiten unter Verwendung von verschiedenen Techniken und Substraten sowie ESEM/EDAX-Untersuchungen durchgeführt.

List of symbols and abbreviations

IL	ionic liquid
API	active pharmaceutical ingredients
ρ	density, $g\ cm^{-3}$
η	viscosity, cP
Λ	molar conductivity, $S\ m^2\ mol^{-1}$
K	conductivity, $S\ m^{-1}$
T	temperature, K
T_g	glass temperature, K
NMR	nuclear magnetic resonance
EMIm	1-Ethyl-3-methylimidazolium
BP	N-Butylpyridinium
DMPI	1,2 Dimethyl-3-propylimidazolium
BMI	1-Butyl-3-methylimidazolium
TPPA	trimethylpropylammonium
TMHA	trimethylhexylammonium
HSLA	high strength low alloy
HEB	hot-electron bolometer
CV	Cyclic voltammetry
WE	working electrode
CE	counter electrode
RE	reference electrode
CA	Chronoamperometry
CP	Chronopotentiometry
DSC	Differential scanning calorimetry
KFT	Karl Fischer titration
ESEM	environmental scanning electron microscope
EDAX	energy-dispersive X-ray analyser
GC	glassy carbon
OCP	open circuit potential
v	scan rate, $V\ s^{-1}$
i	current density, $mA\ cm^{-2}$
i_p^c	cathodic peak current density, $mA\ cm^{-2}$

i_p^a	anodic peak current density, $mA\ cm^{-2}$
E_p	peak potential, V
E_p^c	cathodic peak potential, V
E_p^a	anodic peak potential, V
PR	peak current ratio
n	dissolution valence or number of electrons
I	current, A
Q	electric charge, C
M	molecular weight, $g\ mole^{-1}$
ΔW	anodic weight loss, g
F	Faraday constant, $96485.34\ A\ s\ mole^{-1}$

PART 1. INTRODUCTION

Ionic liquids (ILs) as a relatively new class of solvents have been widely studied in various scientific fields over last decades. Most of ionic liquids are the salts which typically consist of nitrogen containing organic cations and inorganic anions with melting points below 100°C. Historically these compounds can be divided into three categories: a) so-called *first-generation*, which are chloroaluminates ionic liquids; b) *second-generation*, which are air- and water-stable ionic liquids and c) *third-generation*, which are the task-specific and chiral ionic liquids [1-12]. As ionic liquids are made of at least two components (the cation and anion), which can be varied causing a numerous set of properties, they are often called “designer solvents” [13-15].

Ionic liquids possess many useful properties which make them of the fundamental interest to all chemists [16-17], among them: low melting points, negligible vapour pressure, high thermal stability, good ionic conductivity, and large window of electrochemical stability [18-37]. With regard to the above mentioned properties, the areas of application of ionic liquids are growing very rapidly. Ionic liquids are widely used in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications [38-56]. From the viewpoint of electrochemistry, which is the most interesting in present work, ionic liquids are investigated as electrolytes for electroplating of a range of metals impossible to deposit from aqueous baths due to hydrolysis [57-96]. The electroplating of refractory metals such as Ti, Zr, Mo, W, Ta and Nb, which were earlier mainly deposited from high temperature molten salts, at the temperatures below 200°C is still of particular interest. The present study will focus on the electrochemical investigation of niobium, which has a number of unique characteristics, such as very high melting point, excellent strength at high temperatures, high resistance to corrosion, good electrical and heat conducting properties, hardness *etc.*, that makes it useful in numerous of applications [97-121]. Niobium coatings, which are over an order magnitude less expensive than the niobium in metal form, have attracted special attention in aerospace, automotive industries, electronic devices, superconducting magnets and biomedical implants [104-112].

The goal of this thesis was to investigate the electrochemical behaviour of niobium(V) in different pyrrolidinium-based ionic liquids in respect to the possible electroplating of niobium at low temperatures as alternative media to high-temperature molten salts electrolytes. For this purpose the electrochemical investigations were performed and discussed in combination with spectroscopic data. The structure and composition of electrochemically active species of niobium at various oxidation states in ionic liquids was investigated by

means of FTIR and Raman spectroscopy at room temperature and *in situ* at operating temperature (20-200°C). Special attention has been given to the effect of temperature, composition, presence of niobium powder or using niobium soluble electrode as well as additives of alkali metal halides on the reduction of niobium(V) in ionic liquids.

The selection of the systems was guided by results reported for high temperature molten salts from which niobium was successfully electrodeposited. Two ionic liquids consisting of 1-butyl-1-methylpyrrolidinium chloride (Pyr₁₄Cl) as an organic part and NbCl₅ and K₂NbF₇ salts of niobium(V) as inorganic one were examined. The results of the present research were performed as follows: synthesis, spectroscopic analysis of the electrochemically active species, electrochemical behaviour and electroplating experiments for most promising compositions.

The synthesis of novel ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ and (x)Pyr₁₄Cl-(1-x)K₂NbF₇ in a wide range of compositions from x=0.85 to x=0.20 at different temperatures (140-190°C) was achieved. The FTIR spectroscopy and Karl Fischer titration were applied for the quality control of the starting materials (salts of niobium, additives of alkali fluorides) and ionic liquids before each investigation.

The FTIR and Raman spectroscopy were used to obtain the information about the complexes of niobium in different oxidation states in ionic liquids which were formed during mixing of the Pyr₁₄Cl with NbCl₅ and K₂NbF₇ depending on composition. Moreover for detailed investigation of the influence of the temperature on the structure and behaviour of niobium species during electrochemical process the *in situ* Raman measurements (20-200°C) were provided and discussed.

The electrochemical behaviour of the electrolytes was studied by means of cyclic voltammetry, chronoamperometry and chronopotentiometry using various set of electrodes. The combination of electrochemical studies with Raman spectroscopic measurements for the first time enabled a relatively detailed picture of the electrochemical reduction of niobium(V) in the ionic liquids of interest depending on the temperature and composition.

Finally, the electroplating experiments for the most promising systems were performed. The structure and quality of the deposits obtained were analysed using environmental scanning electron microscopy (ESEM) complemented by energy dispersive x-ray analysis (EDAX).

All these aspects were performed in the following parts of this dissertation: part 2 is a literature overview, part 3 gives a detailed discussion of materials and experimental methods used, part 4 presents a discussion of obtained results, and finally part 5 contains a summary.

PART 2. LITERATURE OVERVIEW

2.1. Ionic liquids

2.1.1. History of ionic liquids and their classification

Ionic liquids (ILs) are salts with melting points below 100°C typically consist of nitrogen containing organic cations and inorganic anions. These substances are often called “ionic melts”, “ionic fluids”, “liquid organic salts”, “fused salts” or “ambient temperature molten salts”. These compounds correspond to criteria “designer solvents” since they consist at least from two components which can be varied that causes a numerous set of properties. Ionic liquids are not new class of materials, some of them have been known for many years. The first mention about ethanolanmonium nitrate (m.p. 52–55°C) was reported in 1888 by S. Gabriel and J. Weiner [1]. But, the story of the truly ionic liquids began with the first report of the preparation of ethylammonium nitrate [EtNH₃]-[NO₃] (m.p. 12°C) by Paul Walden in 1914 [2]. This pure salt was formed by mixing of concentrated nitric acid and ethylamine followed by removing of water by distillation.

In the 1950s F. Hurley and T. Wier prepared a room-temperature ionic liquid by mixing two moles of anhydrous aluminum chloride with 1 mole of ethylpyridinium bromide for electrodeposition of aluminum [3]. Unfortunately, these AlCl₃-based ionic liquids were sensitive to oxygen and water and should be prepared and handled under inert atmosphere that restrict their use in many applications. It is important to note that such mixtures are the earliest example in the category of so-called *first-generation* ionic liquids and after that all ionic liquids are often classified historically into three generations. The 1970s and 1980s are characterized by interest to the other members of first-generation ionic liquids, namely aluminum chloride - N-butylpyridinium chloride systems that were described by J. Robinson, R. A. Osteryoung [4] and dialkylimidazolium chloroaluminates ionic liquids that were reported by C. L. Hussey *et al.* [5]. Nevertheless, like it already mention above the hygroscopic nature of first-generation ionic liquids has delayed progress in their use.

Thus, a major breakthrough was the development of air- and water-stable ionic liquids, which are considered as *second-generation* ionic liquids. In 1992, J. S. Wilkes and M. J. Zaworotko prepared and characterized a series of novel air and water stable low melting salts based upon the 1-ethyl-3-methylimidazolium cation (EtMeim⁺) and two anions BF₄ and MeCO₂ which were liquids under ambient conditions [6]. This period is characterised by

increasing of interest to imidazolium based ionic liquids with “neutral” weakly coordinating anions such as hexafluorophosphate PF_6^- , tetrafluoroborate BF_4^- and bis(trifluoromethanesulfone)imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$. Researchers began to use air- and water-stable ionic liquids for a wide variety of applications as battery electrolytes and electrolyte baths for electrodeposition of metals and semiconductors, as solvents for organic synthesis and especially as solvents for catalytic reactions [7-9].

The *third-generation* ionic liquids are the task-specific and chiral (asymmetric, non-superimposable on its mirror image) ionic liquids that arose on the research scene in the early 2000s [10]. These compounds are designed for specific tasks as solvent and/or catalyst to be used in a particular chemical process for example as lubricants, energetic materials (in the case of selective separation and extraction processes), and as more environmentally friendly (greener) reaction solvents, among others. This most recent generation of ionic liquids also involve active pharmaceutical ingredients (API), which are being used to produce ionic liquids with biological activity [11-12].

There are at least one million (10^6) simple ionic liquids which means one million possible simple systems that can be easily prepared in the laboratory. If there are one million possible simple systems, then there are one billion (10^{12}) binary combinations of these, and one trillion (10^{18}) ternary systems possible [13].

Obviously such large amount of the ionic liquids makes their classification difficult. Nevertheless, the ionic liquids can be distinguished from one another using several criteria [14-15]:

- a) the number of components (one- and multi-component systems);
- b) whether anion is organic or inorganic;
- c) the acid-base character of the ion (basic ($[\text{NButyl}_4]\text{F}$), neutral (1-butyl-3-methylimidazolium- BF_4^-) and acidic (pyridinium chloride));
- d) based on the group present (for example imidazolium-, pyridinium-, ammonium-, pyrrolidinium- or phosphonium- based ionic liquids);
- e) based on the solubility (organic, aqueous or bi-phasic);
- f) based on melting point (ionic liquids with melting points below room-temperature, even below 0°C , *e.g.*, 1-ethyl-3-methylimidazolium ethylsulfate (m.p. $<-20^\circ\text{C}$), room-temperature ionic liquids with melting points below 100°C and ILs which have melting points above 100°C , *e.g.*, 1-butyl-1-methylpyrrolinium tetrafluoroborate (m.p. 152°C)).

2.1.2. Physicochemical properties of ionic liquids

As already mentioned above most ionic liquids are salts with melting points below 100°C typically consist of nitrogen containing organic cations and inorganic anions. For the most part they are fluids over a wide temperature range (up to 400°C), with higher viscosities than either aqueous or organic electrolytes at room temperature. Ionic liquids are non-volatile, non-flammable and less toxic, they have high thermal stability, that makes them suitable for multiply applications: chemical synthesis, catalysis, separation technology, and the fabrication of conventional electrochemical devices such as batteries and capacitors [16-17]. It is important to note that physicochemical properties of ionic liquids can be dramatically altered by impurities such as water, organic solvents and chlorine ions [18].

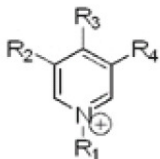
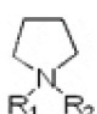
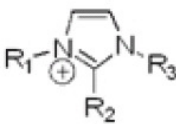
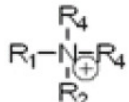
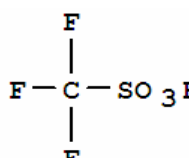
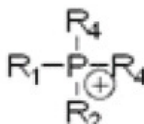
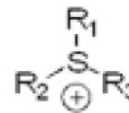
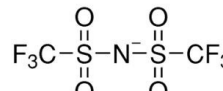
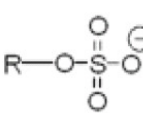
A wide variety of possible anions and cations selection affect the physical and chemical properties of ionic liquids includes: melting point, viscosity, and solubility characteristics [19]. Generally, the cation controls the physical properties of the salt such as its structure and morphology and the anion affects the stability and chemical reactivity as well as the water miscibility of ionic liquid [20, 21].

2.1.2.1. Melting point

The cation of ionic liquid is generally a bulk organic structure with low symmetry, which possesses a low melting point. As the size and the symmetry of the cation increases, the melting point decreases. More often ionic liquids are based on N-alkylpyridinium, N-methyl-N-alkylpyrrolidinium, N-alkyl-N-methylimidazolium or N-alkylammonium cations and the most commonly used alkyl chains in this case are ethyl, butyl, hexyl and octyl. The length of the substituents also affects the melting point of ionic liquid, usually it decreases with increasing of alkyl chain length [22-23].

Also a wide range of anions is employed, from simple halides Cl^- , F^- , Br^- and I^- to inorganic anions such as tetrafluoroborate $[\text{BF}_4]^-$, hexafluorophosphate $[\text{PF}_6]^-$ and to large organic anions like trifluoromethanesulfonate CF_3SO_3^- [24]. In general, the melting point of the salt decreases, as the size of anion increases due to the weaker Coulombic interactions in the crystal lattice. The structures of most commonly used cations and some possible anion types are collected in *Table 2.1*.

Table 2.1. Most commonly used cations and anions

Cations	Anions			
		Hal^- halide	BF_4^- tetrafluoroborate	PF_6^- hexafluorophosphate
			$\text{N}(\text{CN})_2^-$ dicyanamide	
				
pyridinium	pyrrolidinium	trifluoromethanesulfonate		
imidazolium	ammonium	bis(trifluoromethylsulfonyl)imide		
phosphonium	sulfonium	alkylsulfate		

2.1.2.2. Density

Typically, ionic liquids are denser than water, their magnitude of density (ρ) varies in the range of 1.03 to 2.15 g cm^{-3} [24, 25]. The density of ionic liquid also depends upon the choice of cation and anion. For instance, the density of comparable ionic liquids decreases with the increase in the length of the alkyl chain in the cation [26]. Further, the density of ionic liquids is affected by the identity of anions, since the different anions have different densities. For example, within a series of non-haloaluminate ionic liquids containing the same cation species, increasing anion mass corresponds to increasing ionic liquid density [21].

2.1.2.3. Thermal stability and decomposition temperature

Due to the strong Coulombic interaction between ions, and the long range of the interaction, the vapour pressure over the ionic liquid is very low ($10^{-11} \div 10^{-10} \text{ mbar}$). This allows their use in vacuum experiments even at elevated temperature. Such negligible vapour pressure causes the high thermal stability of ionic liquids, some of them are thermally stable up to decomposition temperatures around $350\text{-}400^\circ\text{C}$. In most cases, decomposition occurs

with complete mass loss and volatilization of the component fragments. The decomposition temperature of ionic liquids depends on the composition and highly affected by water content and impurities [27].

2.1.2.4. Viscosity

The viscosity (η) of ionic liquids is high compared to the viscosity of aqueous solutions and high temperature molten salts. Because of the large size of these viscosity units, absolute viscosities of ionic liquids are usually reported in centipoises ($cP = 0.01 P$), where the Poise ($P = g\ cm^{-1}\ s^{-1}$) is the unit of absolute viscosity. Ionic liquid viscosities at room temperature range from a low of around 10 cP to values in excess of 500 cP [24]. The viscosity of many ionic liquids is strongly dependent on temperature, hence increasing the temperature lowers viscosity. Clear, that viscosity of ionic liquid is also affected by the cation and anion nature, as well as impurities present in the media [28].

2.1.2.5. Conductivity

The conductivity of ionic liquids is linked to their viscosity following Walden's rule,

$$\Lambda \eta = \text{constant} \quad (2.1.)$$

where Λ is the molar conductivity, $S\ m^2\ mol^{-1}$ and η is the viscosity, $Pa\ s$. As a class, ionic liquids possess reasonably good ionic conductivities $\sim 10\ mS\ cm^{-1}$, comparable to the best non-aqueous solvent/electrolyte systems. One would expect ionic liquid to have very high conductivities because they are composed entirely of ions. Unfortunately, this is not a case and can be attributed to the reduction of ion mobility resulting from the large ion size found in many ionic liquids [24]. Generally, ionic liquids conductivities are temperature depended, hence increasing of the temperature lowers viscosity and increases conductivity. However, ionic liquids often show a non-linear Arrhenius behaviour of its ionic conductivity in response to temperature. It means that such materials can not be described only by Arrhenius theory, which gives a liner relationship between the logarithm of ionic conductivity and the inverse of temperature:

$$\ln K = A + B\ T^{-1}, \quad (2.2.)$$

where K is conductivity, $S\ m^{-1}$, T is temperature, K , and A and B are material specific parameters [29-30].

Ionic liquids rather follow the empirical Vogel-Fulcher-Tammann (VFT) equation, since they are tended to form glasses below the melting point:

$$K = A \exp \left[-B / (T - T_g) \right] \quad (2.3.)$$

where A and B are fitting parameters and T_g is glass temperature, K [31].

Also, the temperature dependence of ionic liquid's conductivities is strongly affected by the type and size of the ion as well as impurities and presence of co-solvent [28, 32].

2.1.2.6. Transport properties

The behaviour of ionic liquids as electrolytes is strongly influenced by the transport properties of their ionic components [33]. These transport properties relate to the rate of ion movement, as well as the manner in which the ions move (as individual ions, ion-pairs or ion aggregates). Thus conductivity depends on the number and mobility of charge carriers. Therefore, the ion diffusion coefficients and ion transport numbers are two important quantities which are often used to evaluate the transport properties of ionic liquid. There are two methods are commonly used to measure the diffusion coefficients of the ions in ionic liquids, namely electrochemical and nuclear magnetic resonance (NMR) spectroscopic methods [24]. The electrochemical methods measure the diffusion coefficient of an ion in presence of a concentration gradient (Fick diffusion), while the NMR methods measure it in the absence of any concentration gradients (self-diffusion). But, both types of diffusion coefficients under same conditions are equivalent [34-35]. Important to note, that many factors, namely size of ions, shape of ions and magnitude of interactions between cation and anion affect the self-diffusion coefficients of cations and anions in ionic liquids [36].

2.1.2.7. The window of electrochemical stability

One of the most important advantages of ionic liquids is their wide electrochemical windows (up to 5V) over which the electrolyte is stable. It means the electrochemical potential range over which the solvent is electrochemically inert and neither reduced nor oxidized at an electrode surface. This allows the electrochemical deposition of refractory metals and reactive elements such as, for example, Al, Ta, and Si, which in the past were only accessible using high-temperature molten salts or partially organic solvents [37].

Cyclic voltammetry and linear sweep voltammetry are usually used for the electrochemical window estimation of the ionic liquids. Using such techniques, one obtains

the cathodic and anodic potential limits of the ionic liquid toward a certain reference electrode [33]. In case of ionic liquids, it is often used the so-called quasi-reference (or pseudo-reference) metal electrodes such as Pt or Ag wire, that certainly makes difficult to compare obtained data. It must be noted that the electrochemical window of ionic liquid is influenced not only by the electrode materials, but also by the electrochemical stability of the cation, sweep rate of potential, temperature and presence of impurities. One should be careful with contaminations such as halides and especially water, hence even hydrophobic systems takes water from the atmosphere [27, 33].

2.1.3. Electrochemical application of ionic liquids

With regard to the above mentioned multitude of useful properties, the application areas of ionic liquids are growing very rapidly. They are used as “solvents” for organic, organometallic syntheses and catalysis [38], as electrolytes in electrochemistry [39], in fuel [40] and solar cells [41], as lubricants [42], as a stationary phase for chromatography [43], as matrices for mass spectrometry [44], supports for the immobilization of enzymes [45], in separation technologies [46], as liquid crystals [47], templates for the synthesis of mesoporous [48], nano-materials [49] and ordered films [50], materials for embalming and tissue preservation [51], etc.

From the viewpoint of electrochemistry, which is most interesting in present work, ionic liquids are investigated as solvents for technological applications such as metal surface finishing, electrodeposition, batteries, capacitors, fuel cells, electrosynthesis, and nuclear waste treatment [52]. Due to their perfect solvent properties, it is easy to dissolve the salts of plating metals and deposit metallic films with desirable thickness. In contrast to other electrolytes, ionic liquids are non-toxic, non-flammable and have been considered to environmentally friendly, recyclable media. Furthermore, their low vapour pressure allows them to be used in galvanic bath at variable temperatures. The electrochemical deposition of the most technologically important metals has been shown to be possible from a wide range of ionic liquids and will be discussed in details later. Finally, their high ionic conductivity and good electrochemical stability makes them very attractive for electrolytic capacitors, batteries and fuel cells [53-54]. Also, few novel electrochemical applications of ionic liquids, namely treatment of nuclear waste (the removal of Cs^+ from tank waste using a hydrophobic IL) [55] and using them as solvents in electrowetting on dielectric microreactors or lab-on-a-chip systems [56], are found to be interesting for researchers.

2.1.4. Electrochemical deposition of metals from ionic liquids

Despite the lack of reliable models to describe mass transport and material growth in ionic liquids, there are many advantages that ionic liquid solvents have over aqueous baths, organic electrolytes and high temperature molten salts. Some of these advantages include [27]:

- Electroplating of refractory and some other high reactive metals e.g. Al, Ti, Ta, Nb, Mo, W which impossible to deposit from aqueous electrolytes because of their negative potentials comparing with hydrogen reduction potential. For example, the deposition of Al by electrolysis in a low-temperature process has long been a highly desirable goal, with many potential applications, among them the replacing of cadmium coatings with aluminium ones for future aircraft production.
- Opportunity to avoid hydrogen embrittlement of metallic coatings caused by gaseous hydrogen produced during water electrolysis.
- Enabling easier preparation of alloys and the possibility of a much wider range of possible electroplated alloys than in water media due to the much more nearness of ion electrodeposition potentials in ionic liquids.
- High conductivity and better efficiency of ionic liquids will provide significant energy savings in spite of their relatively high costs.
- The replacement of many toxic and hazardous materials currently used in water, e.g. toxic form of chromium(VI), cyanide, highly corrosive and caustic electrolytes.
- Electroplating of nanocomposite coatings and metal coatings on polymers using ionic liquids containing reducing agents.
- Reduction of the operating temperatures below 200°C comparing with electrochemical deposition of refractory metals from high temperature molten salts electrolytes occurring at 600-900°C.

2.1.4.1. Chloroaluminate ionic liquids

The early history of ionic liquids research was dominated by the using of chloroaluminate systems for electrodeposition of metals and alloys [57]. In spite of their hygroscopicity and tendency to produce toxic and corrosive HCl upon undergoing hydrolysis, chloroaluminate ionic liquids gives a possibility to dissolve many kinds of metal salts and to control the Lewis basicity/acidity by changing the composition of AlCl_3 . This leads to a

nomenclature of the liquids in which the compositions with an excess of Cl^- (i.e., $X(\text{AlCl}_3) < 0.5$) are called basic, those with an excess of Al_2Cl_7^- (i.e., $X(\text{AlCl}_3) > 0.5$) are called acidic, and those at the compound formation point ($X(\text{AlCl}_3) = 0.5$) are called neutral [77].

In the acidic ionic liquids, the electrodeposition of Al occurs by the reduction of Al_2Cl_7^- . When the reduction potential of MCl^{m+}_{n-m} is more positive than that of Al_2Cl_7^- , it is possible to obtain the deposits of pure metal. Metal alloys with Al are obtained if the reduction potential of MCl^{m+}_{n-m} is more negative than that of Al_2Cl_7^- . In the case of basic ionic liquids, the metal salt MCl_n acts as a Lewis acid by accepting the Cl^- anions to form a chloro-complex anion MCl^{m-}_{n+m} and the deposits of pure metal can be obtained [33]. A large number of studies on the electrodeposition from chloroaluminate ionic liquids have been reported and the most interesting of them are summarized in Table 2.2.

Table 2.2. The pure metals and alloys electrodeposited from chloroaluminate ionic liquids

Metal/ alloy	Ionic liquid	Reference
Al	EMImCl/ AlCl_3 (40.0/60.0)	[58]
Al-Mo	EMImCl/ AlCl_3 (33.3/66.7)	[59]
Al-Nb	BPCl/ AlCl_3 / NbCl_5 BPCl/ AlCl_3 / Nb_3Cl_8	[60]
Ga	EMImCl/ AlCl_3 (40.0/60.0)	[61]
Sn	EMImCl/ AlCl_3 (33.3/66.7)	[62]
Pb	EMImCl/ AlCl_3 (33.3/66.7)	[63]
Bi	BPCl/ AlCl_3 (33.3/66.7)	[64]
Fe	BPCl/ AlCl_3 (33.3/66.7)	[65]
Co	EMImCl/ AlCl_3 (40.0/60.0)	[66]
Ni	BPCl/ AlCl_3 (40.0/60.0)	[67]
Cu	BPCl/ AlCl_3 (33.3/66.7)	[68]
Zn	EMImCl/ AlCl_3 (40.0/60.0)	[69]
Ag	EMImCl/ AlCl_3 (33.3/66.7)	[70]
Hg	EMImCl/ AlCl_3 (33.3/66.7)	[71]
In	DMPICl/ AlCl_3 (51.0/49.0)	[72]
Ti	EMImCl/ AlCl_3 (60.0/40.0)	[73]
Te	EMImCl/ AlCl_3 (55.6/44.4)	[74]
Pd	EMImCl/ AlCl_3 (55.6/44.4)	[75]
Au	EMImCl/ AlCl_3 (55.6/44.4)	[76]

The organic cations are abbreviated as follows: EMIm – *1-Ethyl-3-methylimidazolium*, BP – *N-Butylpyridinium*, DMPI – *1,2 Dimethyl-3-propylimidazolium*

2.1.4.2. Ionic liquids with BF_4^- and PF_6^- anions

In the developing of ionic liquids for practical applications, it was necessary to investigate non-chloroaluminate ionic liquids, especially those which are against moisture. The electrodeposition of several metals and alloys has been investigated in tetrafluoroborate, BF_4^- ionic liquids, which are considerably moisture resistant in contrast to chloroaluminate ionic liquids. Such ionic liquids are neutral in the concept of Lewis basicity/acidity and metal ions can be introduced simply by dissolving of their tetrafluoroborate salts. The hexafluorophosphate, PF_6^- ionic liquids are similar to the tetrafluoroborate ones, but it should be noted that they are regarded as hygroscopic. A number of studies on the electrodeposition from tetrafluoroborate BF_4^- and hexafluorophosphate PF_6^- ionic liquids have been reported the most interesting of them are summarized in *Table 2.3*.

Table 2.3. The pure metals and alloys electrodeposited from tetrafluoroborate, BF_4^- and hexafluorophosphate, PF_6^- ionic liquids

Metal/ alloy	Ionic liquid	Reference
Ge	BMIPF ₆	[78]
Sb	EMImCl- EMImBF ₄	[79]
In-Sb	EMImCl- EMImBF ₄	[80]
Cu	EMImCl- EMImBF ₄	[81]
Ag	EMImBF ₄	[82]
Cd	EMImCl- EMImBF ₄	[83]

The organic cations are abbreviated as follows: BMI – *1-Butyl-3-methylimidazolium*, EMIm – *1-Ethyl-3-methylimidazolium*

2.1.4.3. Chlorozincate ionic liquids

One of the well investigated ionic liquid is the mixture of 1-ethyl-3-methylimidazolium chloride, EMImCl and zinc chloride, ZnCl_2 which melts around room temperature and is less reactive against water than the chloroaluminate ionic liquids. It is also possible to adjust the Lewis basicity or acidity by changing the ratio of ZnCl_2 , since ZnCl_2 acts as a Lewis acid. In the basic ionic liquid, the predominant ionic species are EMIm^+ , ZnCl_4^{2-} , and Cl^- , thus the cathodic and anodic limit are defined by the reduction of EMIm^+ and oxidation of Cl^- , respectively. Since the ZnCl_4^{2-} cannot be reduced at a potential more positive than the cathodic decomposition of EMIm^+ , the deposition of metallic zinc does not

occur in the basic conditions. In the case of acidic ionic liquid, the predominant ionic species are EMIm^+ , ZnCl_4^{2-} , ZnCl_3^- , Zn_2Cl_5^- and Zn_3Cl_7^- . Therefore, the electrodeposition of metallic zinc as a result of the reduction of the chlorozincate anions is possible in the acidic conditions and defines the cathodic limit of such mixtures. A number of studies on the electrodeposition of metals and alloys from chlorozincate ionic liquids have been reported and the most interesting of them are summarized in *Table 2.4*.

Table 2.4. The metals and alloys electrodeposited from chlorozincate ionic liquids

Metal/ alloy	Ionic liquid	Reference
Zn	EMImCl/ZnCl_2 <i>acidic</i>	[84]
Te	EMImCl/ZnCl_2 <i>acidic</i>	[85]
Fe	EMImCl/ZnCl_2 <i>acidic</i>	[86]
Zn-Fe	$\text{EMImCl/ZnCl}_2/\text{FeCl}_2$	[86]
Co	EMImCl/ZnCl_2 <i>acidic</i>	[87]
Zn-Co	$\text{BPCl/CoCl}_2/\text{ZnCl}_2$ $\text{EMImCl/CoCl}_2/\text{ZnCl}_2$	[88]
Cd, Zn-Cd	EMImCl/ZnCl_2 <i>acidic</i>	[89]

The organic cations are abbreviated as follows: EMIm – *1-Ethyl-3-methylimidazolium*, BP – *N-Butylpyridinium*

2.1.4.4. Ammonium/ $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ionic liquids

In spite of the many advantages of imidazolium based ionic liquids, their cathodic limits (stability of imidazolium cation, *e.g.* EMIm^+) are not sufficient for the electrodeposition of the base metals. Quaternary ammonium salts have a better cathodic stability than imidazolium ionic liquids, but many of them suffer from the disadvantage that their viscosity is often too high to be useful for electrochemical processes. The viscosity can be reduced by a proper choice of the anion, for instance, bis(trifluoromethylsulfonyl)imide $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ or Tf_2N^- , and by making the alkyl chain not too long (six or less carbon atoms). Therefore, many kinds of room-temperature ionic liquids, which can be obtained by combining of various quaternary ammonium cations with $\text{N}(\text{CF}_3\text{SO}_2)_2^-$, seems to be the promising candidates for electrodeposition processes. Such ionic liquids as the supporting electrolytes are not only stable against moisture but also immiscible with water. There are few

reports on electrodeposition of metals using the $N(CF_3SO_2)_2^-$ ionic liquids and they are collected in Table 2.5.

Table 2.5. The metals electrodeposited from ammonium/ $N(CF_3SO_2)_2^-$ ionic liquids

Metal	Ionic liquid	Reference
Li	TMPA/ $N(CF_3SO_2)_2^-$	[90]
Mg	TMHA/ $N(CF_3SO_2)_2^-$	[91]
Zn	TMHA/ $N(CF_3SO_2)_2^-$	[91]
Ni	TMHA/ $N(CF_3SO_2)_2^-$	[91]
Lanthanide	TMHA/ $N(CF_3SO_2)_2^-$	[92]

The organic cations are abbreviated as follows: TMPA – *trimethylpropylammonium*, TMHA – *trimethylhexylammonium*

2.1.4.5. Pyrrolidinium / $N(CF_3SO_2)_2^-$ ionic liquids

Ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ($N(CF_3SO_2)_2^-$) is one of the most suitable for the electrochemical deposition of metals. It possesses such advantages over other ionic liquids as a low melting point (-6°C) and it is liquid at room temperature; a wide electrochemical window (5.4 V); high thermal stability (350°C). The solution of TaF_5 in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide was successfully used for electrochemical deposition of tantalum. Zein El Abedin *et al.* [93-96] reported the deposition of tantalum at 200°C ; however the EDAX spectrum shows the presence of oxygen, together with carbon and sulphur, explained as the traces of ionic liquid at the electrode surface. The XRD pattern of the deposited layer indicated also the presence of Ta_2O_5 , besides crystalline tantalum. When LiF is added to the electrolyte, the obtained layer contains only crystalline tantalum, claimed by the authors, but oxygen is once more detected on the surface and it was attributed to the oxidation of the deposited tantalum film on exposure to air.

Since niobium(V) is isomorphous to tantalum(V), the data obtained on the electrochemical deposition of tantalum from ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide can be helpful in the interpretation of the results of the present research. They will be involved in the discussion later in corresponding section of the results and discussion (4.1.).

2.2. Niobium: properties and applications

2.2.1. Physicochemical properties of metallic niobium

Refractory metals are a class of metals with a melting point above 2000°C. Five elements, namely niobium, molybdenum, tantalum, tungsten and rhenium satisfy the above-mentioned requirements. By the wider definition, the eight additional elements, titanium, vanadium, chromium, zirconium, hafnium, ruthenium, osmium, and iridium with a melting point above 1850°C are also considered to be a part of the refractory metals [97-98].

Niobium is one of the refractory metals which possess a number of unique characteristics, such as very high melting point, excellent strength at high temperatures, high resistance to corrosion, thermal shock, wear and abrasion, good electrical and heat conducting properties, hardness and many other qualities, that makes it useful in numerous of applications [99].

In 1801 Charles Hatchett discovered a new element and named it *columbium* (*Cb*) after mineral columbite in which it was found [100]. There were many doubts that columbium was really a new separate element, but not tantalum which has very similar properties. Much later, in 1844, Heinrich Rose proved that columbium and tantalum are different from each other and suggested the name *niobium* (*Nb*) for the new element (the name comes from Greek mythology after Niobe, the daughter of the Tantalus). Scientists debated for nearly a century over which name to use, however, in 1949, niobium was officially adopted [101].



Figure 2.1. Metallic niobium

Niobium is a transition metal with number 41 in Group 5 of the periodic table. It is a silver-gray, tough, shiny, soft, ductile metal that resembles stainless steel in appearance (*Figure 2.1.*).

Shades of blue, green and yellow are typical due to formation of an oxide layer on the surface in air. Niobium has relatively low density (8.6 g cm^{-3}), nevertheless can maintain its strength at high temperatures [102]. It has a body-centred cubic crystalline structure and its physical and chemical properties are very similar to tantalum. It must be placed in a protective atmosphere when processed, because it tends to react with oxygen (the metal starts to oxidize rapidly in air at 200°C), carbon, halogens, nitrogen, and sulphur at even moderate temperatures. The metal is inert to acids (sulphuric, nitric and phosphoric), even to aqua regia at room temperatures, but is attacked by hot, concentrated acids, for example hydrofluoric acid and hydrofluoric/nitric acid mixtures [103]. Physicochemical properties of metallic niobium are collected in a *Table 2.6*.

Table 2.6. Physicochemical properties of metallic niobium

Standart atomic weight	92.91
Electrons per shell	2, 8, 18, 12, 1
Electronegativity, Pauling scale	1.6
Atomic radius, pm	146
Density, g cm^{-3}	8.6
Melting point, $^\circ\text{C}$	2467
Boiling point, $^\circ\text{C}$	4744
Crystal structure	bcc
Electrical resistivity, microohm cm	14.4
Thermal expansion, ppm/ $^\circ\text{C}$ (room temperature to 1000°C)	7.3
Thermal conductivity, W/ cm $^\circ\text{C}$	0.54
Specific heat, J/g $^\circ\text{C}$	0.26
Tensile strength at 20°C , GPa	0.4-0.7
Young's modulus at 20°C , GPa	130
Vickers hardness, MPa	1320

2.2.2. Applications of metallic niobium and its compounds

2.2.2.1. Niobium coatings

Niobium coatings are over an order magnitude less expensive than the niobium in metal form. Such coatings have attracted the attention due to their ability to withstand thermal stress, while remaining impermeable to corrosive agents for the protection of aerospace alloys (*i.e.*, aluminium alloys). Moreover, the thermal shock resistant property exhibited by niobium makes it an ideal candidate for aerospace trailing edge coatings where hot fluid treatment is used to remove ice accretions [104].

For the automotive industry, the studies are focused on the development of magnesium alloys with improved corrosion resistance and resistance to the vibration under loads. Since pure magnesium is very reactive and corrodes rapidly, the effects of different elements, including niobium, on the formation of protective coatings were studied. The niobium-based coating provides good corrosion resistance which can be attributed to the high stability and excellent paint adhesion. Thus, it is an interesting alternative to the environmentally undesirable Cr(VI)-based coatings for magnesium alloys [105].

Niobium is also applied as a thin protective layer on a stainless steel for use in a bipolar plate component of a polymer electrolyte membrane fuel cell stack. The measurements of the niobium-coated specimen show that the material offers sufficient corrosion resistance as well as pressure-dependent contact resistance [106].

Superconducting properties of niobium thin films for metrological applications in tunnel junctions, diffusion and phonon cooled hot-electron bolometers (HEBs) and radiation sensors have been systematically investigated [107-109]. Electrical and structural properties of niobium films have been measured on a wide range of their thicknesses (10–1000 nm). The experimental data indicate that such devices have good suppression of superconductivity in the contact pads due to the used niobium thin films.

High field super conducting copper cavities coated with thin niobium films are an interesting possible alternative to bulk-niobium ones. They offers several advantages such as better mechanical stability, lower cost, better thermal stability, easier conditioning on the machine, easier connection to the cryostat, less sensitivity to magnetic fields [110, 111].

Niobium coatings were evaluated as a possible surface modification for stainless steel and tissue culture plastic substrates in biomedical implants [112]. One of the surface properties of great importance for orthopedic or dental implants is the corrosion resistance. The corrosion resistance of the metallic materials determines the device service life, but is

also important because of the harmfulness of corrosion products, which can interact with the living organisms. No toxic response was observed for any of the surfaces coated with niobium, indicating that the niobium films act as a biocompatible and bioinert material. In all cases it was demonstrated that the short and long-term biocompatibility of niobium is excellent.

2.2.2.2. Niobium metal plates, sheets, wires and rods

Technical benefits of niobium metal products are the increasing of thermal resistance, oxidation and corrosion resistance, improvement of the creep resistance and reducing of the erosion at high temperatures. They are used in the fabrication of corrosion resistant process equipment including reaction vessels, columns, bayonet heaters, shell and tube heat exchangers, U-tubes, thermowells, spargers, rupture diaphragms, and orifices [113]. Especially, niobium's combination of strength, melting point, resistance to chemical attack, and low neutron absorption cross-section promotes its use in the nuclear industry where high temperatures are reached.

2.2.2.3. Niobium powder

Niobium has a high dielectric constant and is thus able to hold and store electrical charges. Therefore, one of the most important uses of niobium in form of powder is a replacement of tantalum in capacitor production for electronic circuits. Furthermore, niobium is much more abundant and costs substantially less than tantalum [114].

2.2.2.4. Niobium oxide and carbide

Niobium exhibits all the formal oxidation states from +5 down to -1, but its most stable state is +5. Niobium forms oxides Nb_2O_5 , NbO_2 , Nb_2O_3 and NbO . Niobium oxides are mainly used in the manufacture of lithium niobate for the surface acoustic wave filters, camera lenses and ceramic capacitors. Niobium carbide (NbC) is an extremely hard refractory ceramic material commercially used in tool bits for cutting tools [115].

2.2.2.5. Steel production

Niobium is an effective micro-alloying element for steel that improves the grain refining and precipitation hardening of the steel, thereby increasing the toughness, strength, formability, weldability and heat resistance. It is achieved with the addition of only trace

amounts of niobium (less than 0.1%). Niobium not only strengthens steel, but also maintains this strength at high temperatures, so, it is mainly used to produce alloys, for instance HSLA (high strength low alloy). Such products have been identified as the preferred construction materials for the reactors in the space power systems and as the structural components in modern automobiles and pipeline construction [116].

2.2.2.6. Superalloys

Niobium is widely used in nickel-, cobalt-, and iron-based superalloys, which contain up to 6.5% of niobium. Due to niobium high strength and oxidation resistance in combination with low weight, superalloys made with niobium are widely used in automobile and space industry, specifically for rocket nozzles in jet engines (as well as land-based wind turbines) and rockets [117, 118].

2.2.2.7. Superconducting magnets

Niobium becomes a superconductor at very low or cryogenic temperatures (below 9.5 K). It also has the largest magnetic penetration depth of any element. Niobium-tin and niobium-titanium (as a type II superconductor wire) are used to make the coil windings for superconducting magnets. These superconducting magnets are used in magnetic resonance imaging and nuclear magnetic resonance instruments as well as in particle accelerators [119]. Niobium nitride (NbN) also becomes a superconductor at low temperatures and it is used in detectors for infrared light.

2.2.2.8. Hypoallergenic applications: medicine and jewelry

One of the important benefits of niobium and some niobium alloys are physiologically inertness and hypoallergenic properties. They are often used for health products such as dental implants, pacemakers and artificial joints and for jewellery that comes into contact with the skin [120, 121].

2.3. Electrochemistry of niobium

2.3.1. *Electrochemical deposition of niobium from high-temperature molten salts*

2.3.1.1. *Crucial factors in niobium electrolysis*

Niobium is widely used because of its many unique properties: superconductivity, thermal and mechanical stability, high corrosion resistance, physiological inertness, etc. The electrochemical deposition of niobium as well as of other refractory metals such as Ti, Zr, Mo, Ta or W can be achieved only from non-aqueous electrolytes because of their relatively negative deposition potentials [122]. Therefore, the research efforts are confined to ionic media.

High temperature molten salts were found to be efficient baths for niobium electrodeposition. The most essential factors are the following:

- composition of electrolytes, *i.e.* different combinations of alkali metal cations and halide anions as well as different salts of niobium(V), namely NbCl_5 , NbF_5 , K_2NbF_7 ;
- temperature which defines the morphology of the deposits;
- impurities of oxyhalides of niobium(V);
- the formation of insoluble non-stoichiometric niobium sub-halides with mean oxidation state between 2 and 3.

The following achievements have been made:

(1) The most efficient electrolytes were found to be alkali fluoride melts (FLiNaK and binary eutectic mixtures LiF-NaF and KF-NaF) with the additives of NbF_5 [123], but mainly of K_2NbF_7 [124-129].

(2) Numerous studies on the electrochemical reduction of niobium from alkali chloride melts were reported [130-136]. Niobium ions were introduced via NbCl_x ($x=3, 4, 5$) [133-134]; by anodic dissolution of metallic niobium [130-132] or by Nb_3Cl_8 [136].

(3) Alkali fluoride-chloride melts were used as chloride electrolytes with the additive of K_2NbF_7 [137, 139, 140, 142, 143] or alkali fluoride electrolytes with the additive of NbCl_5 [138, 141].

(4) Depending on the temperature, one can obtain dispersive powder, dendrites or dense niobium coatings (above 750°C) [125].

(5) Since the oxyhalide complexes of niobium(V) can perturb the electrochemical reaction and degrade the quality of the deposited metal, impurities of niobium(V) oxyhalides

are a crucial factor for niobium deposition. A few studies were performed to investigate the formation of oxyhalide species of niobium(V) and their influence on the electrochemical behaviour of niobium(V) in high-temperature electrolytes [128, 129, 131, 135, 138].

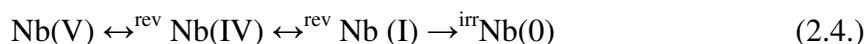
(6) The formation of niobium subhalides such as Nb_3Cl_8 , which can exist in insoluble form and prevent the reduction process of niobium(V) to metal state, was taken into consideration [131-133], but there is a lack of direct confirmation of their existence.

In general, a main disadvantage of molten alkali fluoride and chloride electrolytes are the high operating temperatures at which the substrate can suffer thermal damage and structural changes, and, in particular, corrosion problems play an important role.

2.3.1.2. Electrochemical deposition of niobium from alkali fluoride electrolytes

G.W. Mellors and S. Senderoff [123] have reported the first results on the electrochemical deposition of coherent coatings of niobium on steel from a solution about 10 w/o NbF_5 in a mixture of alkali fluorides LiF-NaF-KF at temperature about 775°C . The properties of the deposited niobium are identical in most respects to metallurgical produced metal of equivalent purity and structure. The major variables are the temperature, valence state, and impurity level. It was shown that the composition is not critical but the presence of a substantially pure fluoride system is required. A tentative explanation based on the maintenance in the solution of a complex anion of appropriate stability for reduction at the cathode to form coherent deposits is advanced.

Later they have studied the mechanism of electrochemical deposition of niobium from a solution of K_2NbF_7 in the LiF-NaF-KF eutectic by means of chronopotentiometry. It was claimed that the reduction of the niobium(V) in fluoride solution takes place in three steps:



The first and the second steps are reversible and diffusion controlled [124]. The first reversible one-electron step to the tetravalent state occurred at -0.11V (referred to the Ni/Ni^{2+} electrode), second reversible three-electron step to the monovalent state at -0.76V , and finally an irreversible one electron reduction to metal at -1.02V .

Electrochemical deposition of niobium from the binary KF-NaF and ternary electrolyte LiF-NaF-KF were characterized and compared with each other by G.P. Capsimalis *et al.* [125]. In this study the observations have been made on the effects of temperature, current density, and additions of K_3CrF_4 , NaBF_4 and K_2TaF_7 (in the range of 5 to 10 wt%) on the structure and efficiency of the niobium deposits. The effect of various additives resulted in

improvements in surface finish, grain size and hardness. Although some correlations was observed between the texture and other properties studied, no attempt was made to study the growth mechanisms during electrocrystallization. Finally, it has been shown that the addition of tantalum and boron to the electrolyte produced deposits with improved properties.

Contrary to the previous reported three step reduction mechanism of niobium reduction, P. Taxil and J. Mahenc [126] have suggested another two-step process:



at potentials of about -0.06V and -0.17V, respectively, referred to the Ni/Ni²⁺ electrode in the K₂NbF₇-LiF-NaF solutions in the temperature range 550-1050°C. They also reported that at higher temperatures (850-1050°C), using nickel cathodes, the intermetallic compounds such as NbNi and NbNi₃ were obtained.

As already mentioned above, the mechanism of the electrochemical deposition of niobium may be changed by the presence of oxide impurities. Therefore, the influence of oxide on the chemical and electrochemical behaviour of niobium ion in molten fluorides was studied by a number of researches [127-129]. For example, electrodeposition of niobium metal from K₂NbF₇-LiF-NaF-KF-Na₂O melts at 700 °C has been investigated and reported by E. Cristensen *et al.* [127]. Cyclic voltammetry showed that NbF₇²⁻ was reduced in two steps and the following mechanism was proposed:



When oxide is present, new waves due to the reduction of niobium mono-oxofluoro and bi-oxofluoro complexes are observed at -0.6V and -0.74V, respectively, referred to the Ni/NiF₂ reference electrode.

It was shown that, when consecutive amounts of Na₂O were added to the molten fluoride solutions, the originally presented NbF₇²⁻ complexes easily form oxofluoride complexes such as NbOF₅²⁻ and NbOF₄³⁻, which changes the reduction mechanism completely. Here it may be noted that for the melt compositions with O/Nb(V) ratios lower than one, pure metal was always deposited.

Practically, two main types of models have been proposed to explain the mechanism of electrochemical reduction of niobium in molten fluoride electrolytes. There are three- and two-step processes respectively:



and



Generally, it was shown that it is necessary to operate molten fluoride electrolytes above 750°C and keep an average valence of niobium ions close to 4.2 and the oxide content as low as possible to obtain dense coherent deposits of niobium.

2.3.1.3 Electrochemical deposition of niobium from alkali chloride electrolytes

In spite of successful use of molten alkali fluoride electrolytes, more recently attempts to produce niobium were carried out from molten alkali chloride electrolytes. Such electrolytes are considered to be less toxic and corrosive than the fluoride ones. Three types of electrolytic bath were mainly studied: NaCl-KCl, NaCl-CsCl and LiCl-KCl.

F. Lantelme, Y. Berghoute and A. Salmi have studied the electrodeposition of niobium by linear sweep voltammetry at a metallic electrode [130]. Two eutectic mixtures LiCl-KCl and NaCl-KCl were used for electroplating experiments. Niobium ions were introduced to the system via dissolution of pure metal working electrode according to the reaction:



and the reduction of the generated ions were studied during the backward sweep.

Later on, F. Lantelme with A. Barhoun, and J. Chevalet have investigated the electrochemical properties of niobium chlorides in the molten eutectic LiCl-KCl in details and determined the fundamental role of the temperature [131]. At temperatures ranging from 380 to 600 °C, two reversible redox reactions were detected:



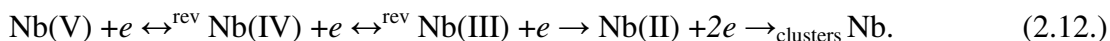
and



Reduction of Nb(III) led to metallic niobium, however the deposition was perturbed by the formation insoluble non-stoichiometric niobium subhalides (mean oxidation state between 2 and 3) at electrode surface. At higher temperatures, above 650°C the perturbing compounds progressively disappear and coherent niobium deposits were obtained. It was also shown that the presence of oxide ions induces the formation of niobium oxides during electrolysis of niobium, since the formation of former usually occurred prior to the metal deposition. Addition of fluoride ions stabilizes the higher oxidation state of niobium ions and seems to have a beneficial influence on the coherence of the niobium deposit.

The mechanism of the electroreduction of niobium chlorides dissolved in molten NaCl-KCl at temperatures ranging from 670 to 870°C was studied by F. Lantelme, Y. Berghoute [132]. Their experimental results indicate that the thin layer of niobium subhalides

(cluster compounds) forms at the metal surface. According to their observation, the electrochemical reduction of niobium chloride can be described by scheme:



It was shown that the presence of fluoride ions stabilizes the upper oxidation states Nb(V) and Nb(IV), whereas Nb(III) species becomes unstable. However, the deposit obtained in fluoride-free bath has a coarse structure with large crystals which tend to form dendrites.

C. Rosenkilde and T. Ostvold have published a series of articles on the detailed investigation of the behaviour of niobium chlorides in the CsCl-NaCl eutectic melt system [133-135]. The eutectic CsCl-NaCl has been chosen as the working bath primarily because it has a low melting point.

In *Part 1*, they have made the electromotive force measurements of NbCl₃ dissolved in the CsCl-NaCl eutectic melt between 600 and 700 °C using niobium metal electrode. Mullite tube containing a silver wire dipping into CsCl-NaCl melt containing 5 mol% AgCl was served as a reference electrode [133]. It was shown that at NbCl₃ concentration below 0.2 mol%, the reversible cell reaction is:

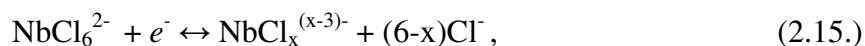


and NbCl₃ seems to be in equilibrium with niobium metal. At higher concentrations, a black deposit contained sodium, caesium, chloride and niobium (mean valence state +3.5) was precipitated on the electrode surface.

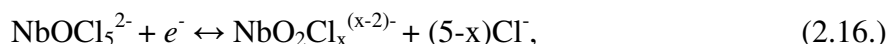
In *Part 2*, the cyclic voltammetry has been used to study the reduction mechanisms of niobium chlorides and oxochlorides in the CsCl-NaCl eutectic melt at temperatures between 823 and 973 K [134]. It was reported that in oxide-free CsCl-NaCl eutectic melt, reduction of Nb(V) chlorides gives Nb(IV) and Nb(III) chlorides according to the reversible and diffusion-controlled reactions:



and



where x = 4, 5 or 6. The reduction products NbCl_x^{(x-3)-} are non-metallic solids at temperatures below about 920 K and metallic niobium above this temperature. In melts saturated with Nb₂O_{5(s)}, the stable niobium oxochlorides are NbOCl₅²⁻, NbO₂Cl_x^{(x-1)-} and NbO₂Cl_x^{(x-2)-}. The reversible and diffusion-controlled reaction in this case is:



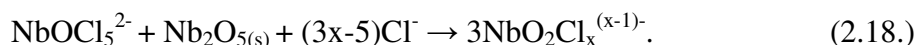
where x = 3, 4 or 5. The reduction products of NbO₂Cl_x^{(x-1)-} and NbO₂Cl_x^{(x-2)-} are probably Nb₂O_{5(s)} and NbO_(s), respectively. Here important to note, that to obtain dense and coherent

niobium metal deposits from the CsCl-NaCl melt, the molar ratio O/Nb must be lower than one, niobium-containing ions must be in equilibrium with niobium metal, and the temperatures must be higher than about 920 K.

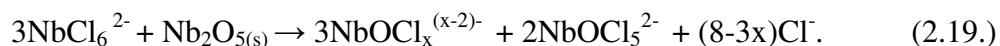
Finally, in *Part 3*, they try to improve the understanding of the behaviour of niobium oxochlorides in molten alkali chlorides [135]. With this aim, the reactions between NbCl_x ($x = 4, 5$) and $\text{Nb}_2\text{O}_{5(s)}$ or $\text{SrO}_{(s)}$ have been studied in the eutectic CsCl-NaCl melt at 650°C. The analysis indicated that NbCl_5 reacted with $\text{Nb}_2\text{O}_{5(s)}$ according to the reactions:



and



NbCl_4 reacted with $\text{Nb}_2\text{O}_{5(s)}$ according to the reaction:



The NbOCl_5^{2-} formed in this reaction reacted further with $\text{Nb}_2\text{O}_{5(s)}$. In the presence of an excess of $\text{SrO}_{(s)}$ at 650 °C, Nb(IV) and Nb(V) form the oxide compounds, $\text{NbO}_{2(s)}$ and $M\text{NbO}_{3(s)}$, where $M = \text{Na}, \text{Cs}, \frac{1}{2} \text{Sr}$, respectively, with very low solubility.

The solubility and electrochemical properties of Nb_3Cl_8 in LiCl-KCl eutectic melt were examined and reported by M. Mohamedi, Y. Sato and T. Yamamura [136]. It was found that the maximum solubility of Nb_3Cl_8 is not higher than 0.8 wt% within the 400-500°C temperature range. At a tungsten electrode, Nb_3Cl_8 is reduced to metallic niobium through two consecutive electrochemical steps: a first reversible step involving one electron charge transfer and a second rather irreversible step implying two electrons number exchange and yielding to metallic niobium. This last step is perturbed by the formation of niobium subhalide insoluble compounds (clusters).

2.3.1.4 Electrochemical deposition of niobium from mixed alkali chloride-fluoride electrolytes

Mixed chloride-fluoride electrolytes were also widely investigated, since they combine the properties of both chloride and fluoride molten salts. Moreover, it was shown that introducing of fluoride ions to the chloride bath stabilizes the higher oxidation states of niobium. Mixed chloride-fluoride electrolytes in its term fall into two conditional categories: solutions of K_2NbF_7 in molten eutectic NaCl-KCl or NaCl-KCl-KF melts [137, 139-140, 142-143] and molten fluoride bath LiF-NaF with NbCl_5 as a source of niobium ions [138, 141].

The mechanism of electrodeposition of niobium from fluoroniobate, K_2NbF_7 solution in molten NaCl-KCl at 720°C was studied by A. Barhoun *et al.* [143]. It was shown that the reaction proceeds in two steps: first a reversible redox reaction,



followed by a quasi-reversible reduction,



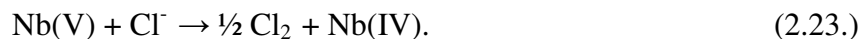
at potentials 0.394V and -0.178V vs. the Ni/Ni^{2+} reference electrode respectively.

The similar two sequential stages:



have been proposed by Polyakova and Taxil [142] as the explanation of the process mechanism in the NaCl-KCl-KF melt with K_2NbF_7 addition at 700 °C. The first stage of cathodic deposition is controlled by diffusion and observed at potential about 0.7V referred to Ag/AgCl reference electrode.

Arurault, Bouteillon and Poignet have shown that the solution of K_2NbF_7 in molten NaCl-KCl (750°C) was not stable and underwent slow chemical reduction to Nb(IV) [137]. This spontaneous process has occurred over several days and could be due to the reduction of Nb(V) to Nb(IV) in the presence of vitreous carbon, or by the chlorine ions according to the reaction:



Therefore, Nb(IV) as the stable species found in the melt, was reduced to Nb via slow four-electron exchange step at around -0.5V vs. AgCl/Ag reference electrode:



The studies of Gillesberg *et al.* [139] have been performed on the system NaCl-KCl-KF with K_2NbF_7 in the temperature range 370-725°C including the studies on the influence of oxide on the redox mechanism of niobium. They have reported that in the temperature range 370-520 °C Nb (V) was reduced to Nb (III) in two reversible steps:



and at these temperatures subvalent halides of niobium were formed at more negative potentials. The metallic niobium was formed only at temperatures above 660°C. It was also suggested that oxide addition mainly leads to precipitation of oxide containing compounds.

Two systems, LiF-NaF-NbCl₅ and the LiF-NaF-NbCl₅ containing oxide, were used by Chamelot *et al.* for electrolytic deposition of niobium at 780 °C [138, 141]. They have stated

that the electrochemical reduction occurs starting from Nb(V) and proposed the following mechanism:



which is in a good agreement with previous authors. Their work shows that it is possible both: to increase the electrodeposition rate of niobium and to avoid the deleterious effects of mass transfer on the surface of the coating. It was also concluded that pulse electrodeposition is a powerful technique for improving the characteristics of plating in mixed alkali chloride-fluoride media.

Similar to the deposition from pure fluoride melts, the valence of niobium ions has to be close to 4, and the oxide ion content should be as low as possible. It should be also noted that, since the reverse disproportionation:



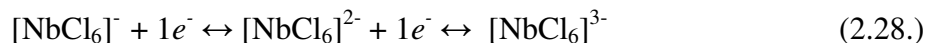
occurs and leads to the dissolution of the deposited niobium, it is necessary to apply the pre-reduced bath using metallic niobium.

2.3.2. Electrochemical reduction of niobium from ionic liquids

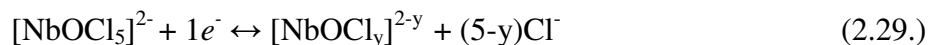
Since the electrochemical deposition of niobium from high temperature molten salts electrolytes is well investigated, the technological processes can be improved only in details. The niobium electrodeposition from ionic liquids at lower temperatures (below 200°C), as an alternative media to high temperature molten electrolytes, allows avoid the thermal damage of substrate during the electrolysis and thus to promote the extension of its application range.

Comparing with the number of publications on electrochemical deposition of tantalum from ionic liquids, including patents [93-96, 144-150], there is a lack of studies on the mechanism of reduction of niobium(V) despite of the significant industrial interest to deposit niobium at temperatures below 200°C. However, corresponding studies on the electrochemistry of niobium in ionic liquids are relatively rare and less clear.

The first article on the electrochemistry of niobium(V) in room temperature molten salts, namely in 1-ethyl-3-methylimidazolium chloride-AlCl₃ (EMImCl-AlCl₃) electrolyte was published by I.W. Sun and C.L. Hussey in 1989 [151]. This ionic liquid is the most widely used ionic liquid for electrodeposition of metals which cannot be obtained from aqueous solution. It was reported that niobium(V) is complexed as [NbCl₆]⁻ in the basic EMImCl-AlCl₃ ionic liquid, and it can be reduced to [NbCl₆]²⁻ and [NbCl₆]³⁻ according to the one-electron reversible redox reactions:



at a glassy-carbone electrode at potentials 0.17V and -0.93V, respectively, in the 44.4/55.6 mol% melt at 40 °C, referenced to aluminium in the 66.7/33.3 mol% melt. The addition of oxide, represented for the convenience as O^{2-} , to solutions of $[\text{NbCl}_6]^-$ in the basic EMImCl- AlCl_3 ionic liquid results in the decrease in the heights of the $[\text{NbCl}_6]^- / [\text{NbCl}_6]^{2-}$ and $[\text{NbCl}_6]^{2-} / [\text{NbCl}_6]^{3-}$ reduction waves and the appearance of a new reduction wave at -0.71V. The voltammetric results allow suggest that $[\text{NbCl}_6]^-$ is turned to a niobium(V) oxide containing species, $[\text{NbOCl}_5]^{2-}$, which can be converted back to $[\text{NbCl}_6]^-$ by using of phosgene gas. Alternatively, the $[\text{NbOCl}_5]^{2-}$ species can be electrochemically reduced to a strongly paramagnetic monomeric niobium(IV) species, which is associated with a single oxide ion, possibly $[\text{NbOCl}_4]^{2-}$ and $[\text{NbOCl}_5]^{3-}$ according to the reaction:



The electrochemical reduction of niobium(V) from ionic liquids was further investigated from the same electrolyte, 1-ethyl-3-methylimidazolium chloride- AlCl_3 electrolyte [152, 153] but only two reduction steps:



were reported. The studies of G.T. Cheek, H.C. De Long and P.C. Trulove [152] were focused on the acidic region of the EMImCl- AlCl_3 ambient temperature ionic liquid. In such system the chloride concentration is extremely low, allowing the existence of niobium species which may be capable of reduction to the metallic state. The detailed investigations of niobium(V) electrochemistry in acidic EMImCl- AlCl_3 melts have shown that the reduction takes place in a series of one-electron, mostly irreversible steps. Such melt apparently does not produce Nb(0) metal at potentials approaching the aluminium deposition potential. The voltammetry is complicated somewhat by the insoluble nature of the niobium(IV) species. It appears that a niobium(III) species is the lowest-valence species which undergoes reduction before onset of aluminium reduction. The electrodeposition of Nb/Al films (containing up to 15% niobium) has been found to be possible only when niobium(V) is reduced to the trivalent state, niobium(III) in a previous chemical reduction by addition of niobium powder to the ionic liquid.

2.4. Spectroscopy of niobium in non-aqueous media

High temperature molten salts such as alkali chloride-, alkali fluoride- and mixed alkali chloride-fluoride electrolytes are the most efficient baths for electrochemical deposition of niobium. The mechanism of electrochemical reduction of niobium, which finally leads to the metal deposition, has been investigated in details and already described in above section of present thesis.

However, a detailed knowledge of the cathodic processes of metal reduction in these melts still is a central point. In order to control the quality of deposits, *e.g.* their coherence, purity and morphology, the information about identity, structure and stability of the complex ions in these media has to be considered. In case of niobium, this is rather complicated due to the large number of different oxidation states and corresponding complex species existing in the melt.

Furthermore, as it has been already mention, the influence of impurities such as oxygen containing contaminants which originate from the trace of moisture that always difficult to avoid, is one of the crucial factors in niobium deposition from molten salts. Spectroscopic methods, especially Raman spectroscopy, provide the valuable information about the composition and structure of complex species, namely halide and oxyhalide complexes, and can be used in combination with electrochemical studies. In order to identify the electrochemically active species of niobium(V), formed in ionic liquids as well as the presence of the undesirable impurities of niobium oxyhalides, it is necessary to analyse the data on the vibrational spectra of niobium compounds in non-aqueous media.

2.4.1. *Niobium(V) chloride complex compounds*

Niobium Pentachloride, NbCl_5 is formed by the action of chlorine on the heated metal; or, less easily, when niobium pentoxide is heated in the vapour of carbon tetrachloride [154]. Electron diffraction data have showed that NbCl_5 in a gas phase exists as a trigonal bipyramide with Nb–Cl links (*Figure 2.2.*) [155].

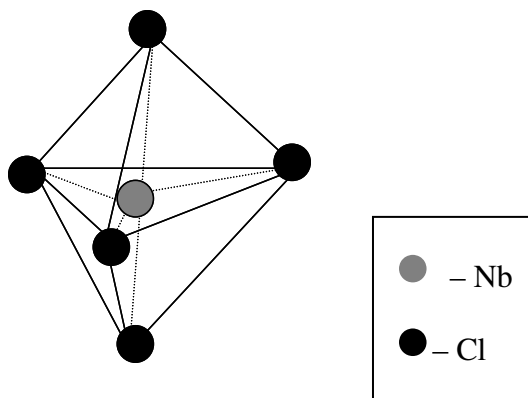


Figure 2.2. The trigonal bipyramid structure of NbCl_5 , where a central gray atom is niobium and the black spheres are chlorine

Niobium pentachloride in a crystal state occurs as a dimer, $\text{Nb}_2\text{Cl}_{10}$. Each niobium atom has six chlorine atoms located about it at the corners of a nearly regular octahedron (*Figure 2.3. a*). The octahedra of the dimer share a common edge, defined by two chlorine atoms bonded to both of the niobium atoms (*Figure 2.3. b*) [156].

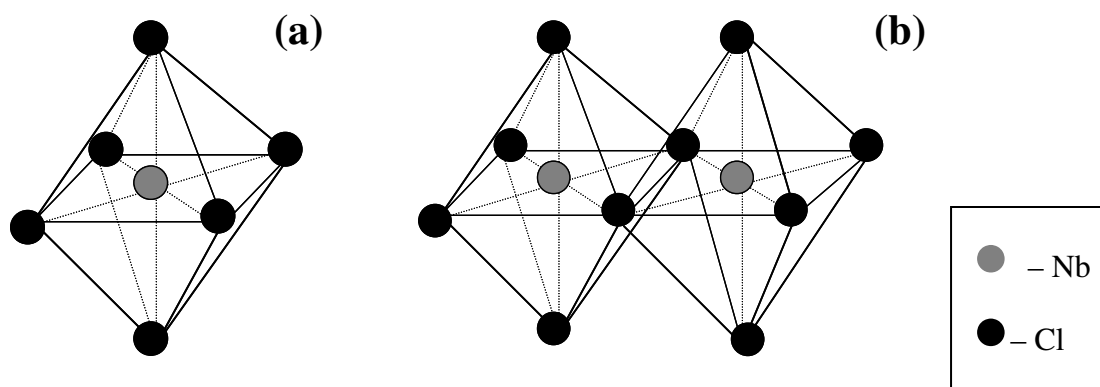


Figure 2.3. Octahedral structure, NbCl_6^- (O_h) (**a**) and the configuration of $\text{Nb}_2\text{Cl}_{10}$ dimer (D_{2h} symmetry) (**b**)

The Raman spectra of molten NbCl_5 were recorded by B. Krebs *et al.* [157] and interpreted as a mixture of monomeric NbCl_5 and dimeric $\text{Nb}_2\text{Cl}_{10}$ ($\text{Nb}_2\text{Cl}_{10} \leftrightarrow 2 \text{NbCl}_5$). The vibrational frequencies of NbCl_5 are collected in *Table 2.7*.

Table 2.7. Raman spectral data for NbCl₅ in molten state (235°C)

The bands in cm ⁻¹	Molecular origin
412 w, p	Nb ₂ Cl ₁₀
393 s, p	NbCl ₅ , Nb ₂ Cl ₁₀
358 w, p	NbCl ₅ , Nb ₂ Cl ₁₀
310 w, dp	NbCl ₅
176 w, dp	NbCl ₅
151 w, dp	NbCl ₅

Key: w = weak; p = polarized; s = strong; dp= depolarized

G.J. Kipouros, J.H. Flint and D.R. Sadoway [158] have presented the Raman spectra of molten alkali metal hexachloroniobate compounds (KNbCl₆ and CsNbCl₆) in the temperature range 723-823 K. Their results confirm that niobium(V) exists in the form of octahedral coordinated complex anion NbCl₆⁻ (*O_h* symmetry) that is stable even in molten state. The Raman spectra of the KNbCl₆ exhibit vibrations at 370 cm⁻¹(s, p), 170 cm⁻¹(m) and CsNbCl₆ at 366 cm⁻¹(s, p), 178 cm⁻¹(m), respectively.

G.A. Voyiatzis *et al.* [159] have investigated the reduction products of pentavalent niobium in molten alkali chlorides by means of *in situ* Raman spectroscopy. The valence states and the species of niobium(V) in alkali chloride melts were identified when different metals were added to the melt. The reduction of niobium(V) to niobium(IV) was observed and the predominant species were found to be NbCl₆⁻ and NbCl₆²⁻ of octahedral structure. These data were used to identify the products of the electrolytic reduction of NbCl₅ in molten alkali chlorides by means of *in situ* Raman spectroelectrochemistry. The frequencies of the Raman bands observed in the solutions at the temperatures up to 930 K are summarized in Table 2.8.

Table 2.8. Raman spectral data for Nb(V) and Nb(IV) chloride complexes in molten alkali chlorides

Molten system	Vibrations, cm ⁻¹	Suggested species
LiCl/KCl _{eut} / 5mol%NbCl ₅	373 p, 174 upper phase	NbCl ₆ ⁻
CsCl/NaCl _{eut} / 5mol%NbCl ₅	370 p, 170	NbCl ₆ ⁻
CsCl / 5mol%NbCl ₅	368 p, 169	NbCl ₆ ⁻
LiCl/KCl _{eut} / 5mol%NbCl ₅ -Nb	373 p, 174 lower phase	NbCl ₆ ⁻
	375 p, 179 upper phase	NbCl ₆ ⁻
	337 p, 153 upper phase	NbCl ₆ ⁻
CsCl/NaCl _{eut} / 5mol%NbCl ₅ -Nb	370 p, 172; 331 p, 157	NbCl ₆ ⁻ ; NbCl ₆ ²⁻
CsCl / 5mol%NbCl ₅ -Nb	369 p, 170; 328 p, 155	NbCl ₆ ⁻ ; NbCl ₆ ²⁻

Key: p = polarized

Numerous spectroscopic investigations were performed on the behaviour of niobium(V) in different chlorine containing media and the most valuable data are summarized in *Table 2.9*. This table presents the Nb-Cl vibrations in different niobium(V) chloride species usually observed in the Raman and IR spectra in various media.

Table 2.9. Raman and/or IR wavenumbers in cm⁻¹ of Nb-Cl vibrations observed in spectra of the different compounds

System				Method
Nb ₂ Cl ₁₀ solid	NbCl ₅ gas phase	CsNbCl ₆ solid	CsNbCl ₆ melt at 873K (NbCl ₆ ⁻)	
Ref. [160]	Ref. [161,162]	Ref. [163]	Ref. [164]	
118 w				Raman
128 w				Raman
168 m	148 w, br	165 s, 174 s	176 m	IR; Raman
189 m	180 w, 184	183 s		IR; Raman
230 vw				Raman
262 m		289 w	288 w	Raman
357 s	317 w	333 s	368 vs	Raman
397 s	394 s, 396	369 vs		IR; Raman
417 vs	430 w			IR; Raman

Key: w = weak; vw = very weak; m = medium; s = strong; vs = very strong; br= broad

To our knowledge, there is a lack of knowledge on the spectroscopy of niobium(V) in ionic liquids. Raman spectroscopy was used to investigate the ionic liquid 1-n-butyl-3-methylimidazolium chloride (BMImCl) with different amounts of NbCl₅, which was published by M.B. Alves *et al.* [165]. In ionic mixtures BMImCl with NbCl₅ the presence of the NbCl₆[−] anions was detected for the compositions at the molar fraction of NbCl₅ in the range 0.4 < x < 0.7. In acidic ionic liquids, a mixture of NbCl₆[−] anions and the neutral Nb₂Cl₁₀ was identified. The presence of NbCl₆[−] is characterized by the features at 179 cm^{−1}, 288 cm^{−1}, and 371 cm^{−1}. The presence of Nb₂Cl₁₀ is confirmed by the Raman vibrations at 171 cm^{−1}, 190 cm^{−1}, 361 cm^{−1}, 396 cm^{−1}, and 417 cm^{−1} that are very similar to those observed for NbCl₅ in a solid state [160]. More detailed description of the structure and composition of niobium chloride species will be given later in corresponding section of the results and discussion (4.1.1.4.).

2.4.2. Niobium(V) fluoride complex compounds

The determination of the crystal structure of potassium heptafluoronioate, K₂NbF₇ showed that it consists of potassium ions and complex ions [NbF₇]^{2−} of C_{2v} symmetry. The lattice structure and the configuration of [NbF₇]^{2−} was defined as a trigonal prism with six F[−] ions at its vertices. The seventh F[−] ion is situated above the centre of the rectangular place of the prism (Figure 2.4.) [166].

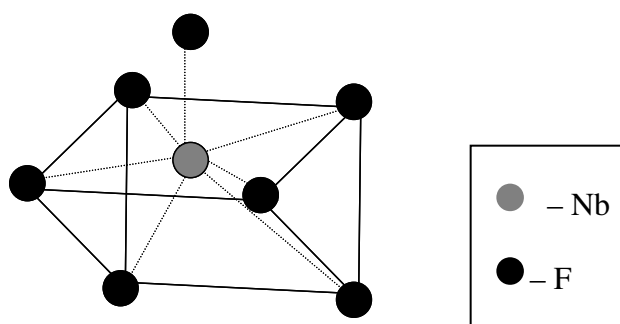


Figure 2.4. Configuration of [NbF₇]^{2−} ion of C_{2v} symmetry

The Raman spectra of K₂NbF₇ dissolved in LiF-NaF-KF eutectic melts were investigated by J.H. von Barner *et al.* [167,168]. The presence of [NbF₇]^{2−} complexes of C_{2v} symmetry was confirmed and the Raman frequencies of such niobium(V) fluoride species were found to be 290, 371 and 626 cm^{−1}.

Contrary to this, solid CsNbF_6 which contains only octahedral NbF_6^- anions (*Figure 2.5.*), is characterized by the Raman vibrations at 280, 562, and 683 cm^{-1} . In the article by O.L. Keller [169], the identification of complex ions of niobium(V) in the solution of K_2NbF_7 in 1 to 50% HF was performed using Raman and IR techniques. The Raman spectra of the solution was compared with the Raman spectra of the crystals of CsNbF_6 , K_2NbF_7 and $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$.

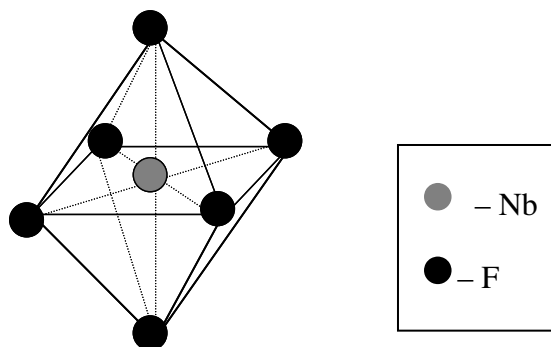


Figure 2.5. Configuration of NbF_6^- ion of O_h symmetry

The IR reflection spectra of molten fluoride solutions of niobium(V) in KF-LiF were obtained and investigated by J.S. Fordyce and R.L. Baum [170]. The IR spectra show two strong bands at 315 cm^{-1} and 555 cm^{-1} and a very sharp medium band at 250 cm^{-1} which were attributed to $[\text{NbF}_7]^{2-}$ ion. This assignment is confirmed by the comparison of these spectra with well characterized IR spectra of solid K_2NbF_7 , demonstrating that $[\text{NbF}_7]^{2-}$ complex ion is the predominant species in these melts.

A. Agulyanski [171] had investigated the alkali fluoride melts with K_2NbF_7 in a wide range of concentrations by means of the IR emission spectroscopy. It was found that niobium(V) species exist in equilibrium between two types of complex ions, $[\text{NbF}_6]^- \leftrightarrow [\text{NbF}_7]^{2-}$. This equilibrium depends on the concentration of niobium(V) and on the nature of alkali metal. The increase of the niobium(V) concentration shifts the equilibrium toward the formation of $[\text{NbF}_6]^-$ ions.

More detailed description of the structure and composition of niobium(V) fluoride species will be given later in the corresponding section of the results and discussion (4.2.3.).

2.4.3. Niobium(V) oxyhalides

Niobium(V) fluoride and especially niobium(V) chloride complexes have a strong affinity to the oxygen. They react with oxide ions which originate from the impurities of the salts during contact with moisture, resulting in the formation of niobium(V) oxychloride and oxyfluoride species. The knowledge about the structure and composition of the various niobium(V) oxyhalides is essential in order to investigate the plating process.

The existence of the complex ion NbOCl_5^{2-} in the solid state $[\text{As}(\text{C}_6\text{H}_5)_4]_2\text{NbOCl}_5 \cdot 2\text{CH}_2\text{Cl}_2$ has been demonstrated by Raman and IR spectroscopy in the studies of U. Müller and I. Lorenz [172]. It was shown that both, the Raman and IR spectra correspond to NbOCl_5^{2-} ion of symmetry C_{4v} . The crystal structure was determined by means of X-ray diffraction. These data confirm that the NbOCl_5^{2-} ion has an octahedral shape with a Nb=O distance of 197 pm. A. Sabatini and I. Bertini [173] have reported the same NbOCl_5^{2-} ions which were investigated by means of far-infrared spectroscopy of the solid RbNbOCl_5 and CsNbOCl_5 . NbOCl_5^{2-} has been also identified in the solution of hydrochloric acid by W.P. Griffith and T.D. Wickins [174].

The Raman spectroscopic evidence of the oxychloro complex ion NbOCl_4^- in the liquid system $\text{CsCl-NbCl}_5\text{-NbOCl}_3$ at temperatures between 340°C and 650°C has been given by C. Rosenkilde *et al.* [164]. The authors have reported that the molten NbOCl_3 shows Raman bands which are typical for the bridging and terminal oxygen. The ions NbCl_6^- , NbOCl_5^{2-} , and NbOCl_4^- have been identified in the basic regions of the system. The structure of ions NbOCl_5^{2-} and NbOCl_4^- as well as NbOCl_3 are presented in Figure 2.6.

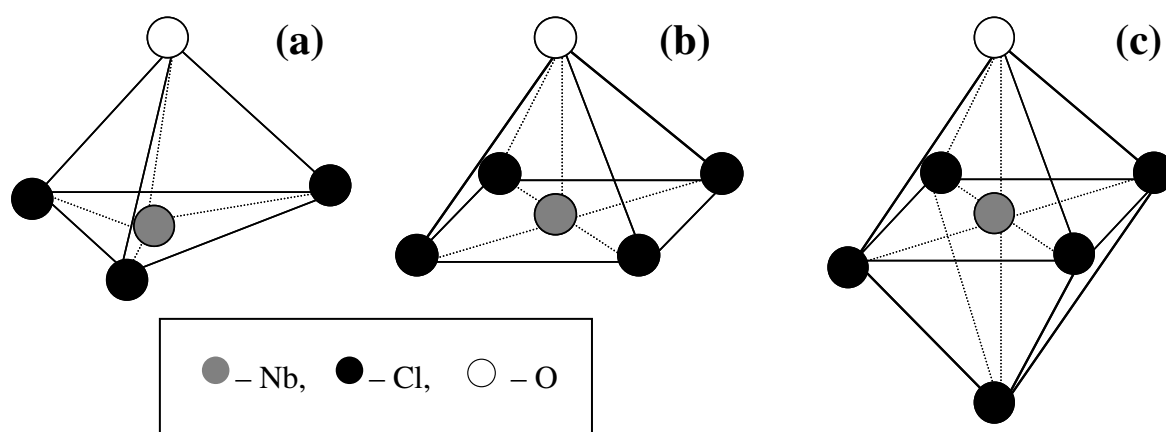


Figure 2.6. The structure of NbOCl_3 (C_{3v} symmetry) (a), NbOCl_5^{2-} (C_{4v} symmetry) (b) and NbOCl_4^- (C_{4v} symmetry) (c), respectively

In the binary system CsCl-NbOCl₃ with excess of CsCl, the equilibrium:



was established. The vibrational frequencies of different niobium oxychlorides are collected in *Table 2.10*.

Table 2.10. Raman spectral data (cm⁻¹) for different niobium oxychlorides

Compound	T, °C	Nb-X breath	Nb=O stretching	Nb-O-Nb symmetric stretching	Ref.
NbOCl ₃ solid	25	421		770, 850, 800	[175]
NbOCl ₃ gas	330	395	993		[175]
NbOCl ₅ ²⁻	25		920		[172]
NbOCl ₄ ⁻	25		960		[176]

The Raman spectra of K₂NbOF₅·H₂O dissolved in water were reported by O.L. Keller [169] and they demonstrate the existence of NbOF₅²⁻ ions. The presence of the NbOF₅²⁻ ions was also confirmed in the molten system LiF-NaF-KF-K₂NbF₇ at 650°C with the addition of small amounts of oxide [168]. NbOF₅²⁻ species are characterized by the vibrations at 921 cm⁻¹, 583 cm⁻¹, and 307 cm⁻¹. Infrared spectra of solidified melts support the existence of a niobium-oxygen double bond, Nb=O in this complex. The vibrational spectrum is in accordance with the band pattern of monomeric NbOF₅²⁻ with a C_{4v} symmetry.

Later on, the existence of the complexes NbOF₅²⁻ and NbO₂F₄³⁻ was established by J.H. von Barner *et al.* [167] in the paper on the complex formation of niobium(V) in eutectic LiF-NaF-KF melt with K₂NbF₇ and with the addition of oxide. Raman spectra indicate the formation of mono oxyfluoro NbOF₅²⁻ (307, 583(p) and 921(p) cm⁻¹) and dioxyfluoro NbO₂F₄³⁻ (284, 360, 815(p) and 878(p) cm⁻¹) complexes with C_{4v} and C_{2v} symmetry, respectively.

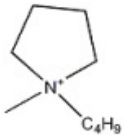
PART 3. EXPERIMENTAL

3.1. Materials

3.1.1. Chemicals

High purity chemicals and starting materials were used in present studies since the impurities play a crucial role in the processes investigated. 1-Butyl-1-methylpyrrolidinium chloride (Pyr₁₄Cl) (Merck, high purity, content of moisture < 100 ppm, mp 203°C) is a white powder which starts to decompose after melting at ~ 210°C. Selected properties of the 1-butyl-1-methylpyrrolidinium chloride used for synthesis are presented in *Table 3.1*.

Table 3.1. Selected properties of the 1-butyl-1-methylpyrrolidinium chloride

Short names	Cation category	Anion category	Molecular weight (g/mol)	Appearance	Melting point (°C)	Decomposition temperature (°C)	Miscibility with water	Molecular formula
bmpl Cl Pyr ₁₄ Cl BMPC	Pyrrolidiniums 	Halides Cl ⁻	177.72	Solid, white powder	203	>210	totally miscible	C ₉ H ₂₀ ClN

NbCl₅ (niobium pentachloride) is a yellow powder (99.995%, ampoule-packed) purchased from Aldrich Chemical Company. The ampoule was opened in MBraun Star glove box (content of O₂ and H₂O below 1-3 ppm) and used without preliminary purification. K₂NbF₇ (potassium heptafluoronioate), 99.5% purity was obtained from Alfa Aesar and used as received. KF, RbF, CsF (potassium, rubidium and caesium fluorides, respectively) were purchased from Aldrich Chemical Company. Chemical and physical properties of the salts which were used for synthesis of ionic liquids are collected in *Table 3.2*.

Table 3.2. Selected properties of the inorganic salts

Substance	Chemical formula	Molar weight (g/mol)	Form	Melting point (°C)	Boiling point (°C)	Density (g/cm ³)
Niobium pentachloride	NbCl ₅	270.17	yellow powder	205	254	2.75
Potassium heptafluoroniobate	K ₂ NbF ₇	304.10	white powder	>700	-	3,21
Potassium Fluoride	KF	58.10	white powder	859	1505	2.48
Rubidium Fluoride	RbF	104.47	white powder	833	1410	3.20
Cesium Fluoride	CsF	151.90	white powder	682	-	4.64

3.1.2. Control of the quality

Pyr₁₄Cl were dried under high vacuum (0.002mbar) at 85-95°C with intensive stirring during 12-24 hours to remove residual moisture (*Figure 3.1.a*). The temperature was kept 85-95°C to avoid the decomposition of ionic liquid. After drying procedure Pyr₁₄Cl was transferred and stored in an argon filled glove box (Lab Star MBraun) with water and oxygen content below 1-3 ppm (*Figure 3.1.b*).

Our long time experience testifies that the storage of ionic liquids in a closed bottle in the glove box does not give a guarantee that ionic liquids will remain dry. The increase of the content of moisture in ionic liquids can occur due to unexpected increase of moisture level in the glove box. Therefore the regular drying of ionic liquids stored in the glove box is the necessary procedure. The quality of ionic liquids was controlled by means of FTIR spectroscopy and Karl Fischer titration (see below Part 3.2.).



Figure 3.1. Vacuum line (a) and Lab Star MBraun argon filled glove box (b)

3.1.3. Synthesis of ionic liquids

The mixtures $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ and $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ form liquids in a wide range of compositions, $x=0.85-0.20$ at different temperatures. To prevent undesirable influence of oxyhalide complexes of niobium(V), the synthesis were carried out under atmosphere of argon in a glove box. The mixtures were prepared by combining of 1-butyl-1-methylpyrrolidinium chloride (Pyr_{14}Cl) with a corresponding amount of NbCl_5 and K_2NbF_7 as well as with the additives of alkali fluorides, KF , RbF , CsF . They were mixed in a mortar, placed in the Pyrex tubes and melted in an electrical furnace in a glove box under stirring (Figure 3.2.). After melting, the samples were quenched and stored in a glove box.

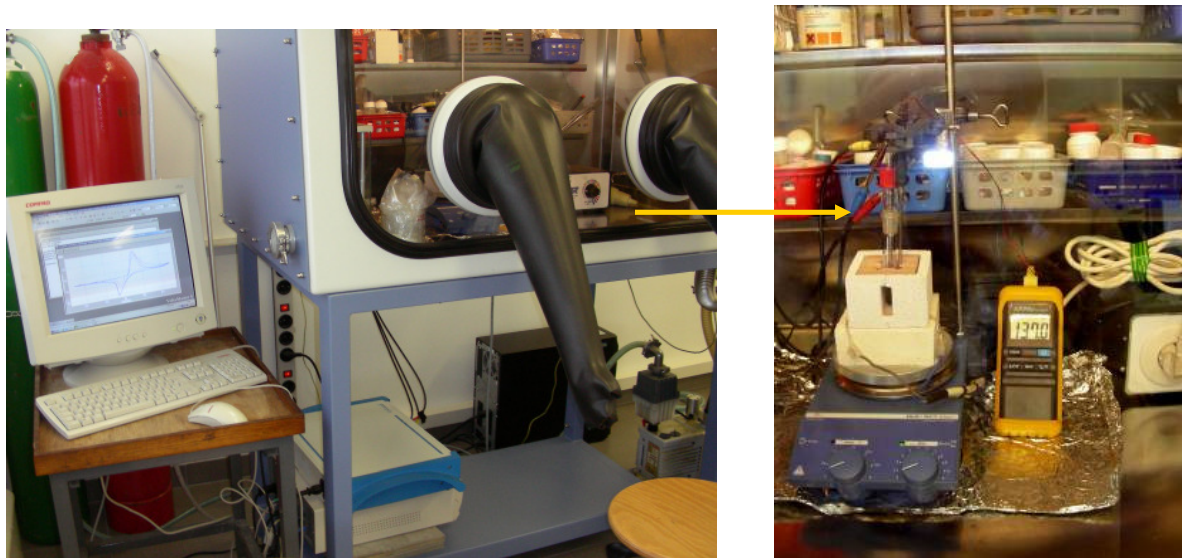


Figure 3.2. Electrical furnace with temperature control and stirrer placed in a glove box

The detailed description of the synthesis of different types of ionic liquids will be given in the corresponding parts of the thesis.

3.2. Methods of studies

3.2.1. Electrochemical methods

Electrochemical measurements were conducted in the argon-filled glove box using the potentiostat Voltalab 40 model PGZ 301 (Radiometer). Duran tubes placed in the electrical furnace were used as electrochemical cells. The electrochemical characterization and electrodeposition experiments were conducted in two different types of electrochemical cells: cyclic voltammometric studies in three electrodes cell (*Figure 3.3. a*) and deposition experiments in two electrodes cell (*Figure 3.3. b*).

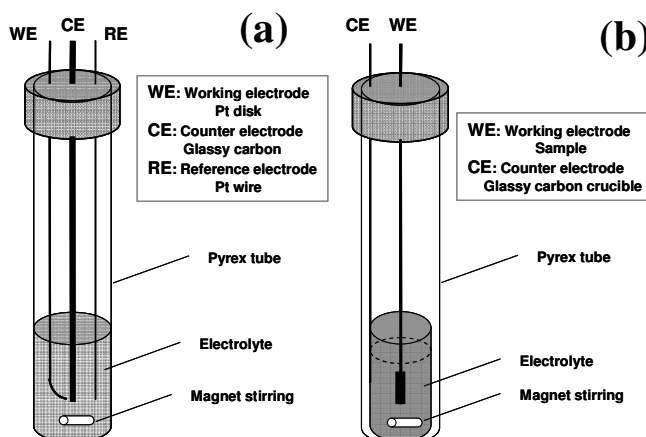
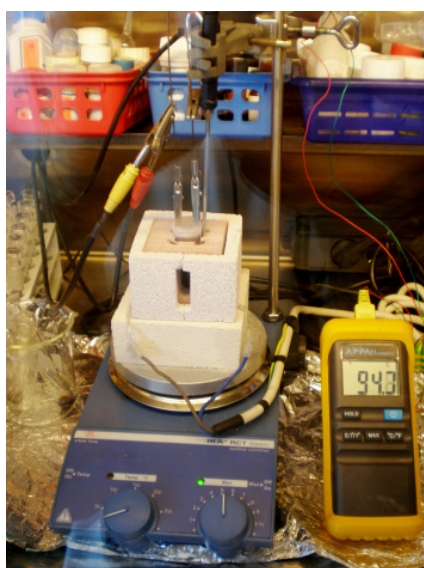


Figure 3.3. Electrical furnace with three electrodes cell for cyclic voltammometric studies (a) and two electrodes cell for deposition experiments (b)

Cyclic voltammetry (CV) is a simple, rapid, and powerful method for the characterization of the electrochemical behaviour of the species that can be electrochemically oxidized or reduced. CV consists of the cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode [177].

The working electrode was a platinum disc (platinum wire Ø 0.5 mm sealed in Duran). Glassy carbon rod (Ø 3.0 mm) was used as a counter electrode. A platinum wire immersed in the electrolyte served as a quasi-reference electrode (*Figure 3.4.*). Niobium wire (Ø 1.0 mm) was used as a working or counter electrode in certain measurements. Cyclic voltammograms were started at the potential of 0 V where the current was zero; in general 5 cycles were recorded.

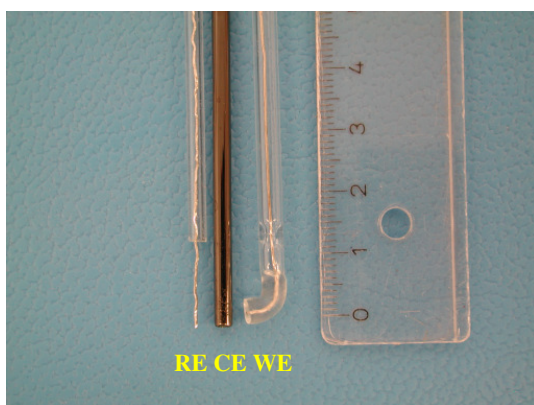


Figure 3.4. Electrodes from left to right: *quasi*-reference electrode (Pt wire), counter electrode (glassy carbon), working electrode (Pt disk)

Chronoamperometry (CA) is the potential step technique, consists basically in applying a constant potential to the working electrode and recording the current as a function of time. *Chronopotentiometry* (CP) is the galvanostatic analogue to chronoamperometry. A constant current is applied to the cell while recording the potential of the working electrode as a function of time. Both techniques are very useful for electrodeposition and other applications [178].

The constant current and pulse-interrupt deposition experiments were carried out on glassy carbon, gold, platinum, silver, stainless steel and nickel substrates in a two-electrode cell. The substrates (cathodes) have a working area less than 1 cm² and distance between cathode and anode was controlled about 3-5 mm according to the experimental cell geometry. Glassy carbon crucible (Sigradur, volume 2 ml) was served as a counter electrode (anode) and as the container for the electrolyte (*Figure 3.5.*).

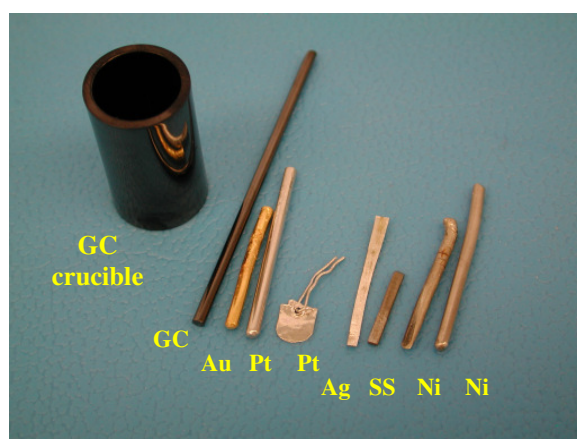


Figure 3.5. Electrodes from left to right: counter electrode (glassy carbon crucible); working electrodes (glassy carbon rod (GC), gold rod, platinum rod, platinum chip, silver, stainless steel, nickel plate and rod)

3.2.2. *In situ Raman spectroscopy*

Raman spectroscopy is a powerful technique which provides the information about the molecular vibrations that can be used for sample identification and quantitation. The electromagnetic radiation absorbed, emitted or scattered by the molecule is analysed. The method involves irradiation with monochromatic light source (*i.e.* beam of radiation from a laser) of a sample and detecting the scattered light [179].

Raman spectra were recorded using a Raman spectrometer Labram Aramis Vis (Horiba Jobin Yvon) with BX41 microscope (True Confocal Aperture with 10x, 50x and 100x objectives). The excitation source was one of the three lasers: an internal He-Ne red laser 633 nm with nominal output power ~ 20 mW, external blue laser 474 nm or green laser 532 nm with nominal output power ~ 50 mW (*Figure 3.6*). The Raman spectra were obtained in the frequency range corresponding to $4000\text{-}100\text{ cm}^{-1}$. The 1-20 sec exposure time usually gave good quality Raman spectra for niobium species.

The samples for Raman measurements were placed in Duran tubes (outer $\varnothing$ 3.0 mm and inner $\varnothing$ 1.5 mm) in the glove box and the tubes were sealed. The samples sealed in Duran tubes were pre-melted to obtain compact substances for the measurements of Raman spectra.

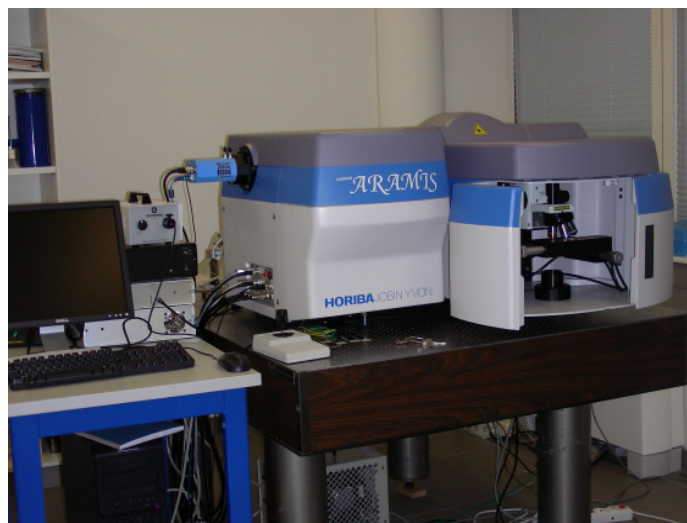


Figure 3.6. Raman spectrometer Labram Aramis Vis (Horiba Jobin Yvon) with BX41 microscope

Raman spectra in the temperature range $20\text{-}210^{\circ}\text{C}$ were recorded using an assembly designed specifically for the project. It consists of a small natural stone furnace with a compartment for the samples and a thermocouple (*Figure 3.7*). The objective of the Raman spectrometer is protected by an optical quartz plate (thickness 0.5 mm).

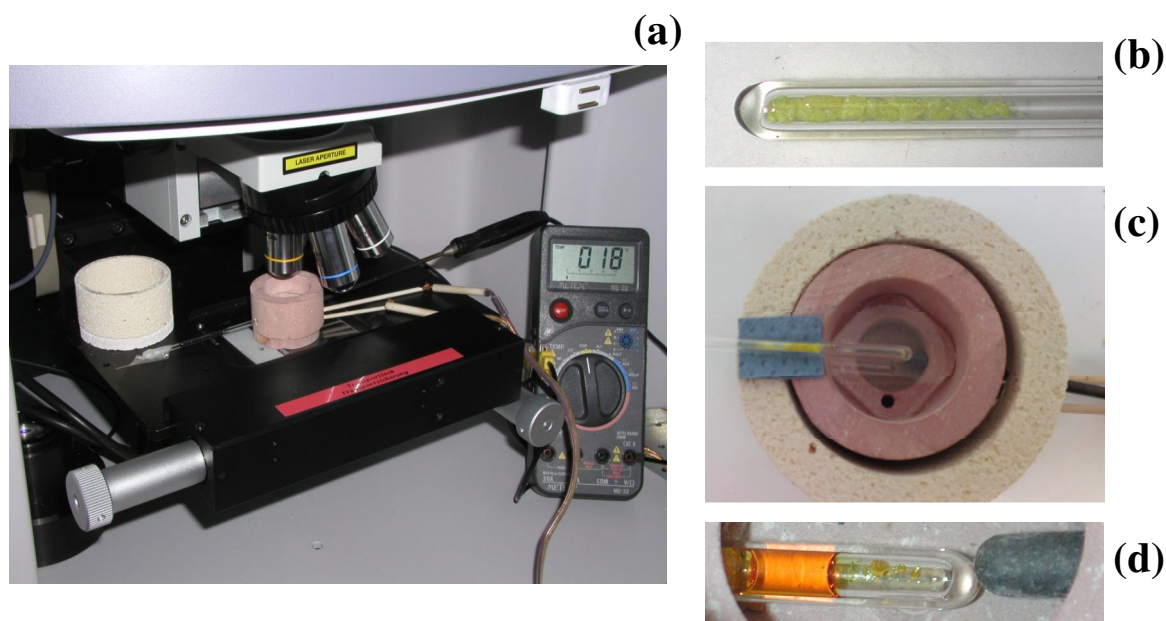


Figure 3.7. Assembly for *in situ* Raman measurements: (a) – general view; (b) – sealed Pyrex tube with NbCl₅, 20°C ; (c) – furnace; (d) - melt of NbCl₅, 210°C and thermocouple

3.2.3. FTIR spectroscopy

FTIR (Fourier transform infrared spectroscopy) is an intensively used technique for materials analysis which can result in a positive identification (qualitative analysis) of different substances. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms forming the material. Since each different material is a unique combination of atoms, there are no two compounds which produce the exact same infrared spectrum. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present [180].

FTIR internal reflection spectra of the quenched samples were recorded using a Bruker FTIR spectrometer Equinox 55 (MKII Golden Gate Single Reflection ATR System with Diamond Top Plate and KRS-5 lenses) with a MCT-nitrogen cooled detector in the range 200-4000 cm⁻¹ at the room temperature (64 scans min⁻¹) (Figure 3.8.).

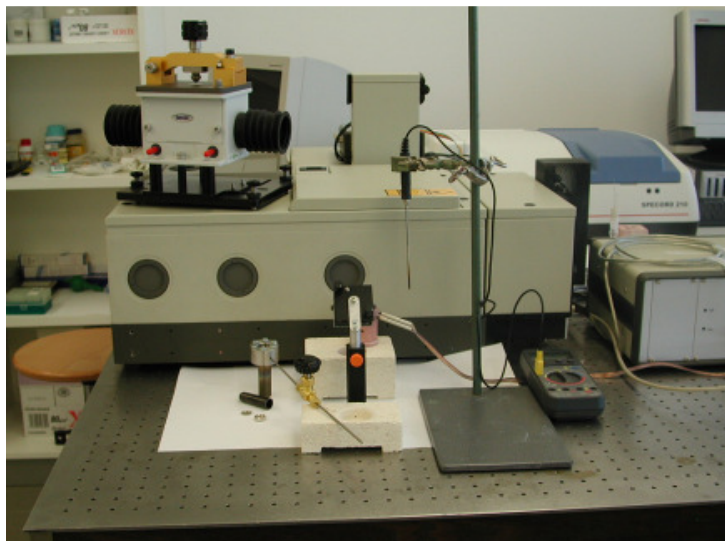


Figure 3.8. Bruker FTIR spectrometer Equinox 55

3.2.4. Supporting methods

3.2.4.1. Karl Fischer titration

Coulometric *Karl Fischer titration* (KFT) is a method for determining the water content in different matrices, based on a selective reaction between water and the Karl Fischer reagent [181]. In comparison to other water detection methods, Karl Fischer titration is less time-consuming and often more accurate. KFT is based on the stoichiometric reaction of water with iodine and sulphur dioxide in the presence of a short-chain alcohol ($R' = \text{CH}_3, \text{C}_2\text{H}_5$) and an organic base (RN), according to the following equation:



The water content of ionic liquids after drying was determined by KFT using a Coulometer 756 KF (Metrohm) calibrated with Hydranal 100 ppm Water Standard (NIST SRM 2890 traceable) and was typically below 7-8 ppm (*Figure 3.9.*).

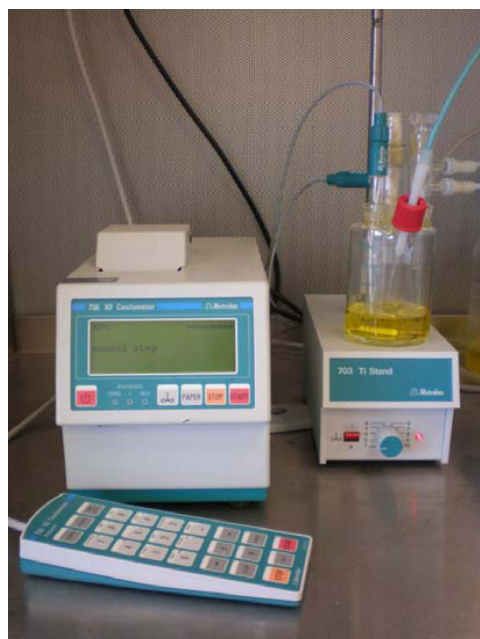


Figure 3.9. Metrohm 756 KF Coulometer

3.2.4.2. Surface characterization (ESEM/EDAX)

The surface morphology was analyzed by an environmental scanning electron microscope (ESEM-FEG, Philips XL 30 with field emission gun, manufactured by FEI, Netherlands) equipped with an energy-dispersive X-ray analyser (EDAX, Phoenix System supported with Genesis software) for characterisation of the chemical composition (*Figure 3.10.*).



Figure 3.10. Environmental scanning electron microscope (ESEM) with an energy dispersive X-ray analyser (EDAX)

Images were taken with a secondary electron (SE) detector for giving an impression of the surface at high lateral resolution, as well as with a backscattered electron (BSE) detector, which produces an elemental contrast image of the surface. Hence, surface structure and elemental composition can be combined, and interdependencies can be investigated by SEM/EDAX analysis. The samples were inspected using 10 kV acceleration voltage at magnifications of 50x, 500x, 1000x and 5000x each.

PART 4. RESULTS AND DISSCUSSION

4.1. Ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅

4.1.1. Spectroscopic analysis and electrochemical studies of ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ using standard Pt/Pt/GC electrode system

4.1.1.1. Introduction

This chapter presents the results on the study of electrochemical behaviour of niobium(V) in the basic and acidic ionic liquids (x)1-butyl-1-methylpyrrolidinium chloride-(1-x)NbCl₅ in combination with Raman and FTIR spectroscopic data. The standard three electrodes system was used for electrochemical investigations, namely Pt disk as a working electrode, glassy carbon as a counter one and Pt wire as a quasi-reference reference. Special attention was paid to the effect of the composition and temperature on the electrochemical active species of niobium(V) in these melts.

The electrochemical behaviour of niobium chlorides in molten alkali chloride molten salt systems was investigated in details and already described in literature overview (*section 2.3.1.3.*). The 1-butyl-1-methylpyrrolidinium chloride was used as a model system with a simple Cl⁻ anion which potentially may form the series of the ionic liquids with NbCl₅ that resemble the high temperature alkali chloride melts.

The electrochemical behaviour of the basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80, 0.60, and 0.40 was investigated in details over the temperature range 90-160°C in respect to the electrochemical deposition of niobium and discussed in combination with *in situ* Raman spectroscopic data. It was shown that the mechanism of electrochemical reduction of niobium(V) depends strongly on the structure and composition of the electrochemical active species of niobium(V) defined by the molar composition.

4.1.1.2. Synthesis

The mixtures $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ form liquids in a wide range of compositions $x=0.85-0.20$ at different temperatures. The compositions for electrochemical studies ($x=0.80, 0.60$, and 0.40) were prepared by combining Pyr_{14}Cl with a corresponding amount of NbCl_5 ; they were mixed, placed in Pyrex tubes and melted in an electrical furnace in a glove box (Mbraun Star, O_2 and H_2O content below 3 ppm) under stirring.

The synthesis of the ionic liquid $\text{Pyr}_{14}\text{Cl}/\text{NbCl}_5$ with a molar ratio of $0.80/0.20$ occurs at $\sim 60^\circ\text{C}$ and is accompanied by insignificant gas evolution. The colour of the liquid during the synthesis changed from dark-orange to dark brown-greenish. The most easily formed and transparent liquids were obtained for $\text{Pyr}_{14}\text{Cl}/\text{NbCl}_5$ molar ratios of $0.60/0.40$ and $0.40/0.60$ at $\sim 60-70^\circ\text{C}$ and $\sim 120^\circ\text{C}$, respectively. The ionic liquid with a molar ratio of $0.60/0.40$ is deep-orange. For the acidic ionic liquid ($x=0.40$), a small precipitation of yellow powder was observed on the walls of the tube during the heating due to the partial volatility of NbCl_5 ; the ionic liquid is deep-orange-brown. After melting, the samples were quenched.

The visual experimental observations are presented in *Figure 4.1*. This diagram is the presentation of the state of the mixtures (temperatures when the mixtures are getting liquid, transparent liquids etc.) versus composition (molar fraction of the components) under the constant pressure.

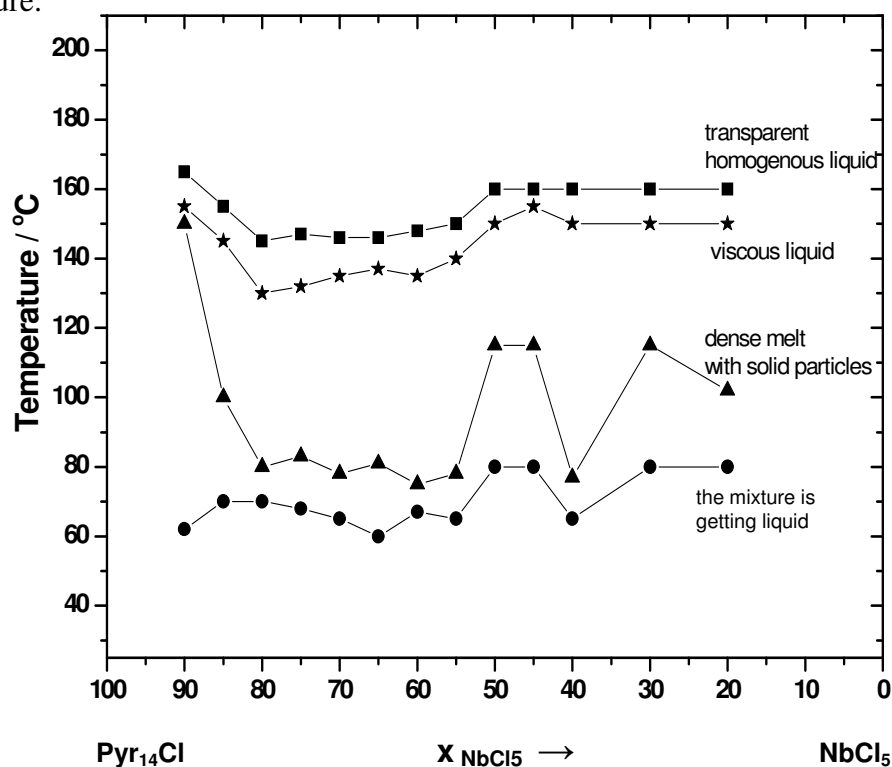


Figure 4.1. Two components diagram for system $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.80-0.20$

4.1.1.3. FTIR spectroscopy of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$

Small amount of each mixture was placed in vitreous tube and the FTIR spectra were recorded at the same day. The FTIR spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ with the molar fraction of Pyr_{14}Cl in the range from $x=0.85$ to 0.20 are presented in *Figure 4.2*.

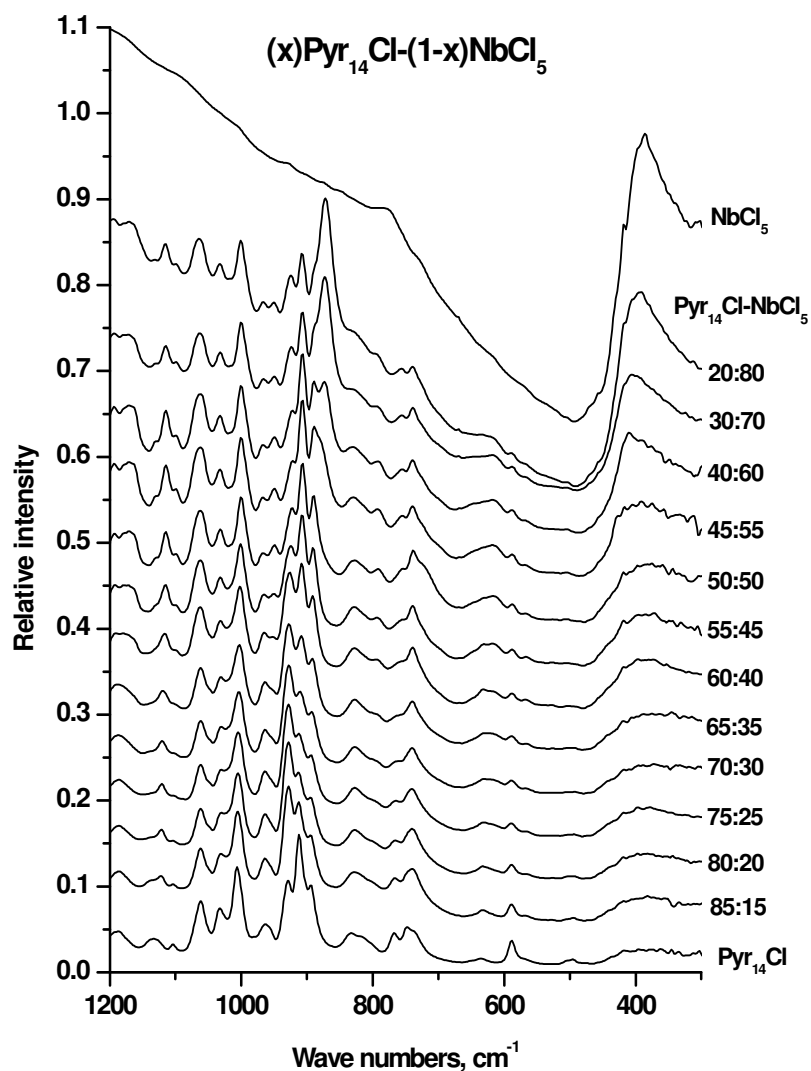


Figure 4.2. FTIR spectra of the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.85$ - 0.20 : concentration dependence

More detailed view for compositions at $x=0.80$ and $x=0.60$, as well as a FTIR spectrum of pure 1-butyl-1-methylpyrrolidinium chloride Pyr_{14}Cl are shown in *Figure 4.3*.

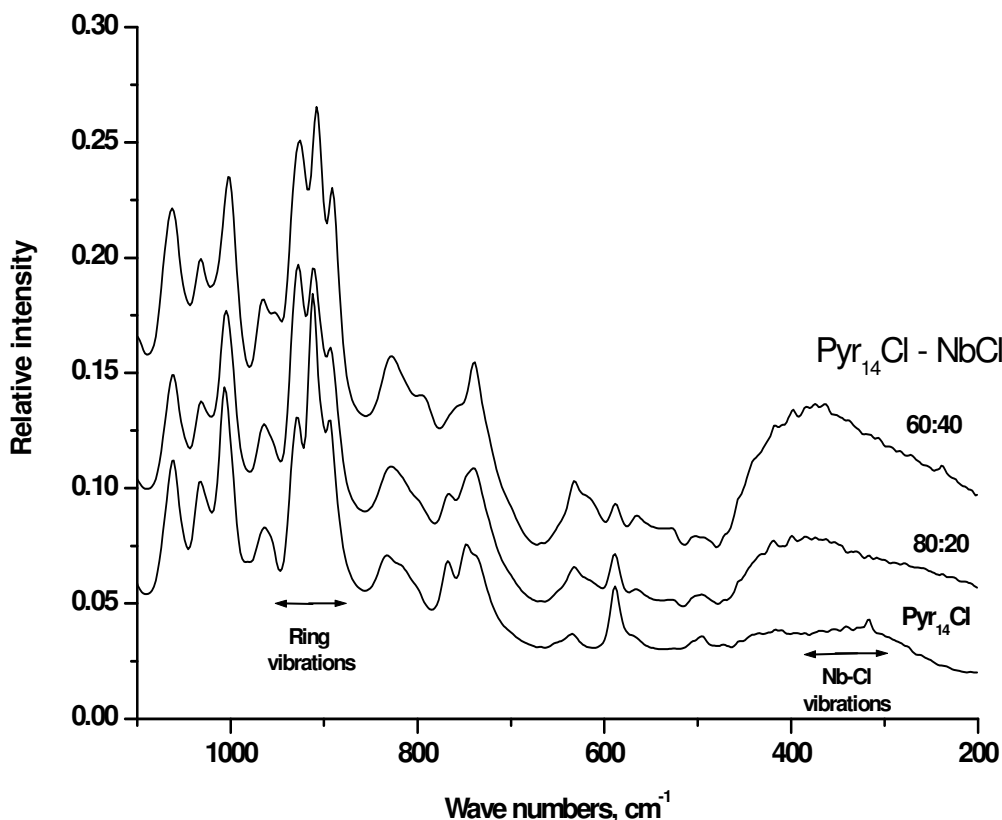


Figure 4.3. FTIR spectra of the pure Pyr_{14}Cl and $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ mixtures at $x=0.80$ and $x=0.60$

FTIR spectra of the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ mixtures at different molar ratios demonstrate that the most pronounced changes are observed in the range of symmetric ring breathing mode $890\text{--}940\text{ cm}^{-1}$ (ring internal vibrations). These reflect the changes of the vibration features of the pyrrolidinium ring as the molar fraction of Pyr_{14}Cl decreases in the mixtures. As the large niobium(V) species replace the smaller Cl^- anion, it causes the transformation of the mutual space orientation between pyrrolidinium ring and the inorganic species.

Insignificant changes of other vibrational modes of Pyr_{14}Cl are also observed in the ionic liquids. The vibrations of Nb-Cl bond are observed in the range $300\text{--}450\text{ cm}^{-1}$ as a very broad band. A broadening of the Nb-Cl band with simultaneous decrease in its intensity is observed in the FTIR spectra, as the molar fraction of NbCl_5 decreases in the mixtures. However, the exact structure of the niobium species which are responsible for this vibration cannot be determined by means of FTIR spectroscopy. Therefore it should be proved by Raman spectroscopy as more appropriate technique.

4.1.1.4. Raman spectroscopy of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$

The Raman spectroscopy was used to obtain the information about the complexes of niobium(V) in the basic and acidic range of the compositions. As niobium may exist in different valence states, Raman spectroscopy was also used to identify the possible formation of niobium species in lower oxidation states. The corresponding Raman spectra are presented in Figure 4.4.

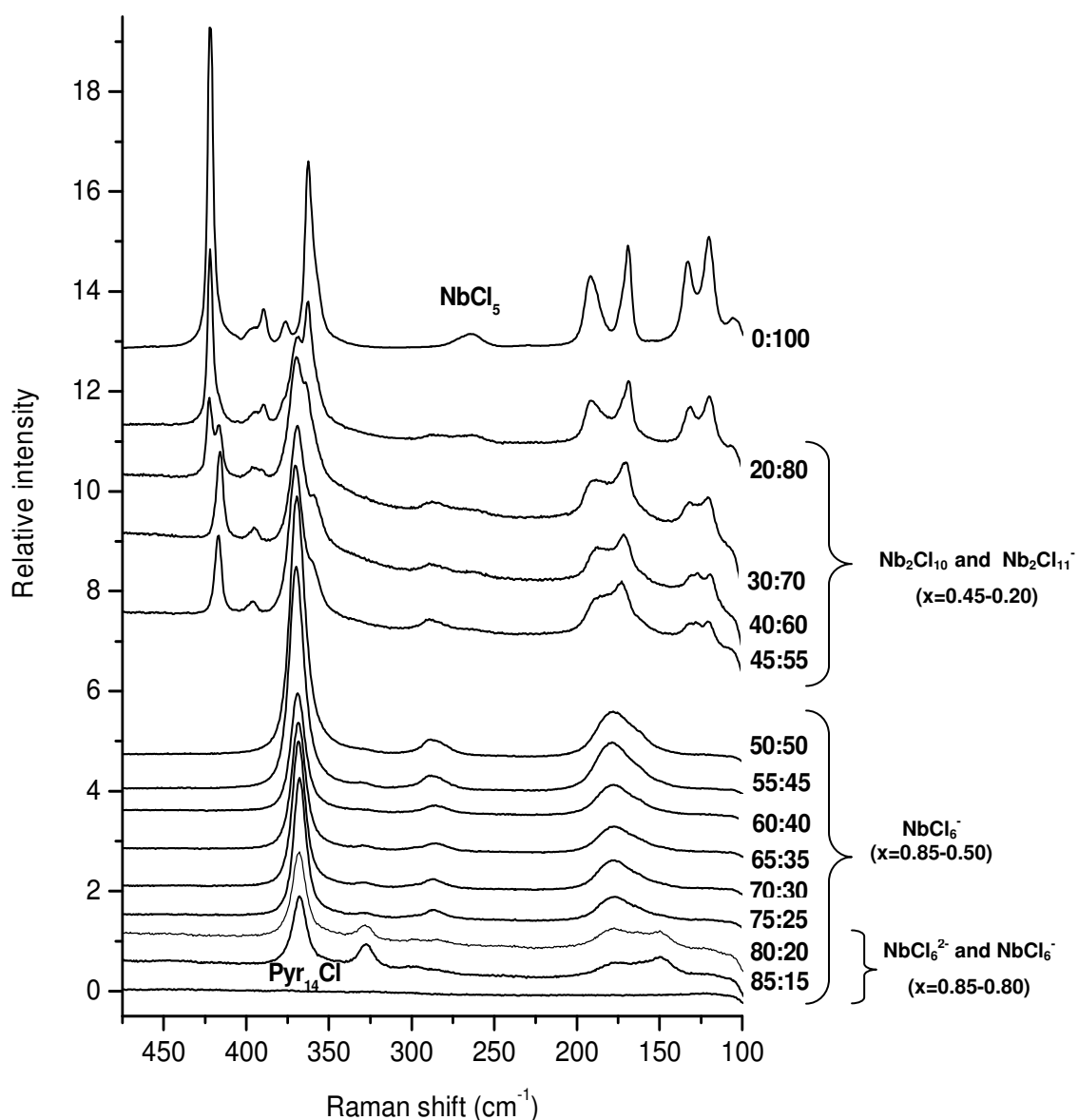


Figure 4.4. Raman spectra of the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.85-0.20$: concentration dependence

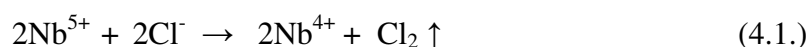
According to the Raman data, in basic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.85-0.80, the self-reduction of niobium(V) to tetravalent state was observed and octahedral species NbCl₆⁻ and NbCl₆²⁻ were identified. In the range of compositions x=0.85-0.50, niobium(V) exists as the octahedral complexes NbCl₆⁻. In acidic mixtures at x=0.45-0.20, the niobium(V) species are present in the form of Nb₂Cl₁₀ and Nb₂Cl₁₁⁻.

Because of the different structure and composition of electrochemically active species (ECAS) of niobium(V) in the basic and acidic ionic liquids, three systems were chosen for electrochemical measurements: at x=0.80, x=0.60, and x=0.40. Moreover, for detailed investigation of the influence of the temperature on the species of niobium(V, IV) during electrochemical process, *in situ* Raman measurements were provided and discussed in the section 4.1.1.5.

4.1.1.5. *In situ* Raman spectra of basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅

In situ Raman spectra of the ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ for x=0.80; 0.60; 0.40 in the temperature range 20-120°C are presented in *Figure 4.5. a-c*.

The Raman spectra of the basic (x)Pyr₁₄Cl-(1-x)NbCl₅ mixture at x=0.80 (*Figure 4.5. a*) exhibit vibrations at 178 cm⁻¹(s), 294 cm⁻¹(w, br), and 380 cm⁻¹(s) which are the characteristic bands for the octahedral complex NbCl₆⁻ (O_h) [162, 182-184]. The additional bands observed at 327 cm⁻¹ and 150 cm⁻¹ can be assigned to the octahedral species NbCl₆²⁻ (O_h) which are formed according to the following self-reduction reaction in excess of Cl⁻ anions :



This reaction in alkali metal chloride melts has been studied by different electrochemical methods [134, 185, 186] by Raman spectroscopy [182, 184] and NMR spectroscopy [184] and it was found that the kinetics of the reaction depends on temperature and the composition of the melt. In chloride melts the concentration of Nb⁴⁺ species decreases with increasing amount of NbCl₅, as well as in the corresponding fluoride melts containing NbF₅ [137, 187].

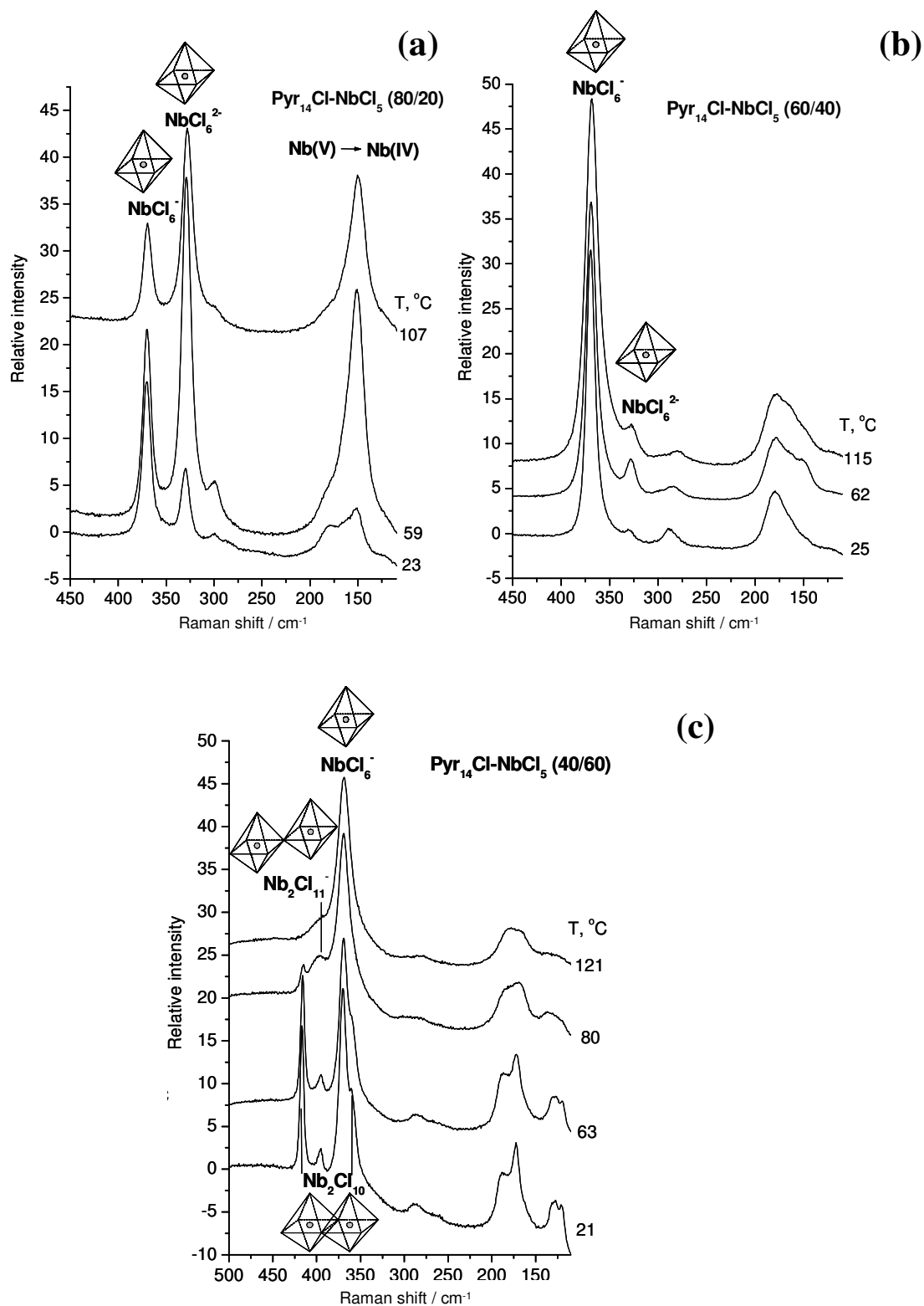


Figure 4.5. *In situ* Raman spectra of basic (a) - molar ratio 80/20, (b) - molar ratio 60/40 and acidic (c) - molar ratio 40/60 ionic liquids (x) Pyr_{14}Cl -(1-x) NbCl_5 (20-120 $^{\circ}\text{C}$) and the structure of the corresponding electrochemical active species of niobium

The same behaviour is observed in ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅. At x=0.80 the increase of the temperature leads to the gradual shift of the equilibrium between NbCl₆⁻ and concentration NbCl₆²⁻ complexes towards Nb⁴⁺ species. Distribution of Nb⁵⁺ and Nb⁴⁺ species depending on the temperature was estimated on the base of the evaluation of the Raman spectra by computer-resolving the bands into sums of Gaussians functions and is presented in *Figure 4.6*. At room temperature 70 % of the species exist as Nb⁵⁺ and 30 % as Nb⁴⁺ and at 110°C the opposite situation is observed: ~ 25 % of Nb⁵⁺ and ~ 75 % of Nb⁴⁺.

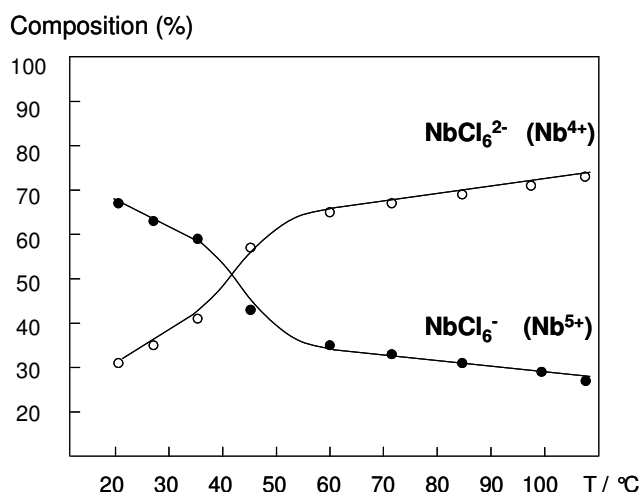


Figure 4.6. Distribution of Nb⁵⁺ and Nb⁴⁺ containing complexes versus temperature in the ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ (x=0.80) evaluated by computer resolving the peaks into sums of Gaussian functions

As the concentration of NbCl₅ increases, the tendency to self-reduction Nb⁵⁺ → Nb⁴⁺ is suppressed and only a negligible amount of NbCl₆²⁻ complexes is identified on the basis of Raman spectra (*Figure 4.5 b*). This phenomenon is correlated with acidity/basicity of ionic liquids and the loss of the free Cl⁻ anions as the mole fraction of NbCl₅ increases. Increase of temperature does not initiate the shift of equilibrium between NbCl₆⁻ and NbCl₆²⁻ complexes towards Nb⁴⁺ species as it was observed for the composition x=0.80, it remains practically constant.

The Raman spectrum of the acidic ionic liquid for x=0.40 at room temperature is very similar to the spectrum of pure NbCl₅ (*Figure 4.5. c*) [157,161,162,188] and NbCl₅ in some alkali halide mixtures known from the literature [182,184]. Niobium (V) species consist of binuclear octahedral species Nb₂Cl₁₀ (416 cm⁻¹) sharing a common edge. The evolution of the Raman spectra with temperature reflects the changes of the structure of these dimeric species and above 80°C the equilibrium between NbCl₆⁻ (369 cm⁻¹) and binuclear Nb₂Cl₁₁⁻ (396 cm⁻¹) octahedral species has to be considered, see also [184].

4.1.1.6. Cyclic voltammetry in basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅: general overview

On the basis of *in situ* Raman spectra of basic and acidic ionic liquids, (x)Pyr₁₄Cl-(1-x)NbCl₅, the structure and composition of electrochemically active species, as well as the valence states of niobium(V, IV) at operating temperatures are defined and these data will be important for the interpretation of the mechanism of electrochemical reduction of niobium (V). Cyclic voltammograms of basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ recorded on Pt disk working electrode using glassy carbon as counter and Pt wire as quasi-reference electrodes are presented in Figure 4.7. They demonstrate the significant changes in the mechanism of electrochemical reduction depending on composition and temperature of the electrolytes.

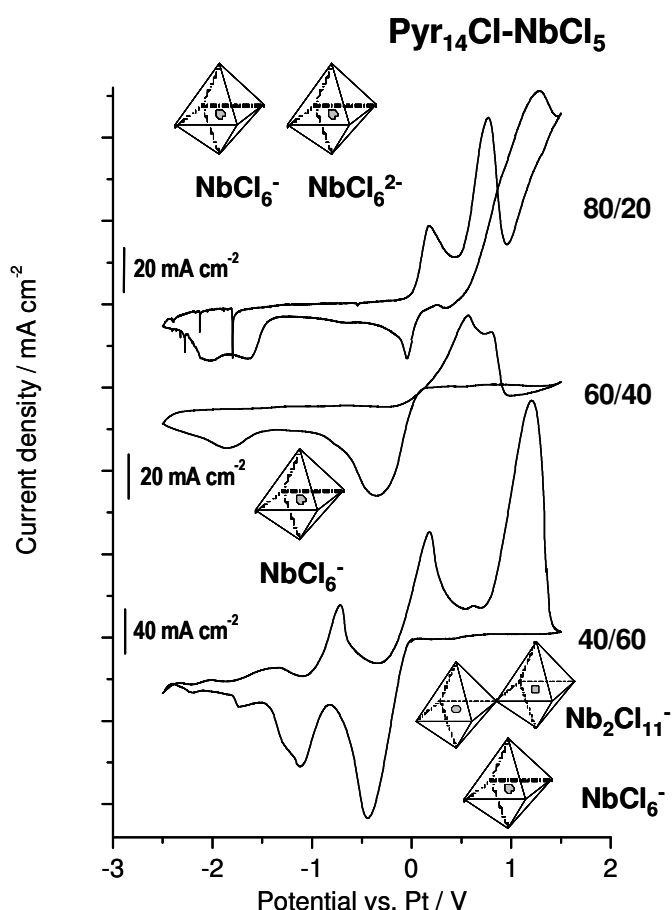


Figure 4.7. General view of cyclic voltammograms of basic and acidic ionic liquids, (x)Pyr₁₄Cl-(1-x)NbCl₅, at x=0.80, 0.60, and 0.40 (T=135-145°C; WE-Pt disc; CE-GC; RE-Pt wire; scan rate 100 mV s⁻¹)

4.1.1.7. Cyclic voltammetry of basic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅: composition dependence

The open circuit potential (OCP) of the working electrode with respect to the quasi-reference platinum electrode was about 0 V and was automatically used as the initial potential. These ionic liquids have a wide window of electrochemical stability about 4 V. Cyclic voltammograms of basic ionic liquids in potential range between -2.5V and 1.5V at x=0.80-0.60 are presented in *Figure 4.8*. and they demonstrate the gradual changes of the mechanism of electrochemical reduction of niobium(V) which is correlated in basic ionic liquids with the co-existence of octahedral species of niobium in different valence states, Nb⁵⁺ and Nb⁴⁺, as was confirmed by *in situ* Raman spectroscopy.

According to the Raman spectra, in the ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 and 0.75, the content of Nb⁴⁺ species is significant and they are the dominant ones at the operating temperatures. Beginning from x=0.70, the dominant species are Nb⁵⁺ with an negligible amount of Nb⁴⁺ octahedral species. The electrochemical data are in agreement with the spectroscopic ones and exactly between x=0.75 and x=0.70 one can observe a clear first reduction peak near -0.2 V (*Figure 4.8. b*). In order to investigate in more detail the mechanism of electrochemical reduction of niobium (V), further studies concentrated on two basic ionic liquids, namely at x=0.80 and 0.60.

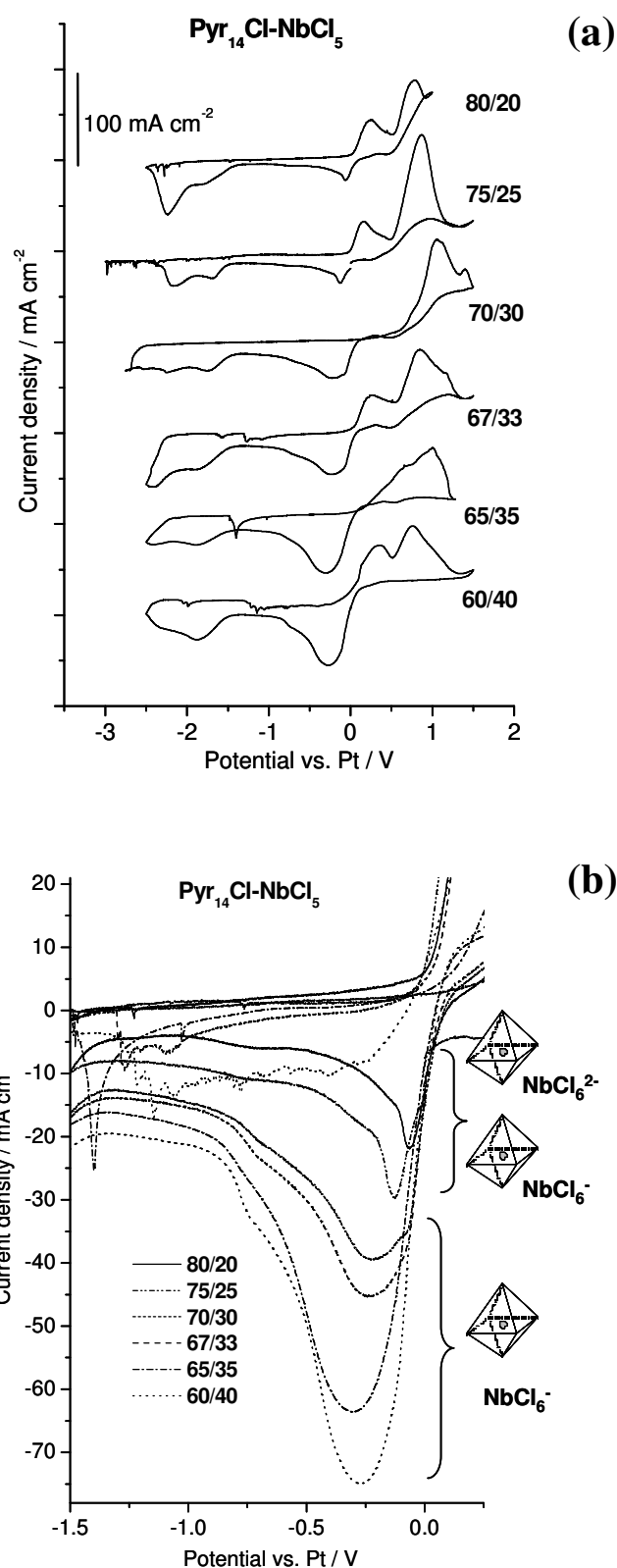


Figure 4.8. Composition dependence of cyclic voltammograms of the (x)Pyr₁₄Cl-(1-x)NbCl₅ ionic liquids in the range of compositions x=0.80-0.60 (T=135-150°C; WE-Pt disc; CE-GC; RE-Pt wire; scan rate 100 mV s⁻¹): general view (a) and in enlarged scale for the first reduction peaks (b)

4.1.1.8. Cyclic voltammetry of basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80

The viscosity of ionic liquids in comparison with high temperature molten salts is very high which defines the transport properties and the kinetics of the reduction processes. So, the investigation of the electrochemical behaviour of electrolytes as a function of temperature provides valuable information about the optimal operating temperatures, *i.e.* the optimization of the deposition parameters.

Cyclic voltammograms of ionic liquids at x=0.80 depending on temperature are presented in *Figure 4.9*. This shows that the current density increases significantly with temperature in the range 130-150 °C. This must be due to the rise of mobility of the electrochemically active species which leads to an increase of the redox reaction rates.

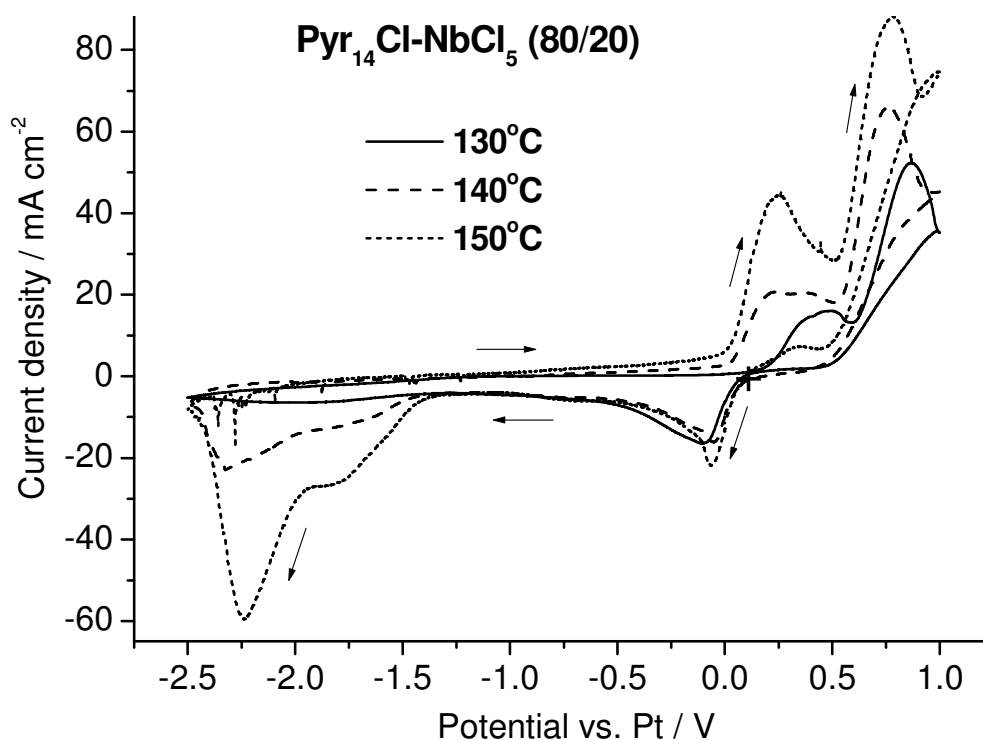


Figure 4.9. Temperature dependence of cyclic voltammograms of the (x)Pyr₁₄Cl-(1-x)NbCl₅ ionic liquids at x=0.80 (WE-Pt disc; CE-GC; RE-Pt wire; scan rate 100 mV s⁻¹)

At temperatures below 130-135°C, the viscosity of the electrolyte is still high and the cyclic voltammograms exhibit no pronounced reduction waves. In the temperature range 135-145°C, a clear growth of the peak currents appears and this range was found to be an optimal one. To testify the range of thermal stability of ionic liquids, DSC (differential scanning calorimetry) measurements of ionic liquids of interest have been performed. It was found that at $x=0.80$ the decomposition is starting above 180°C.

In order to study the correlation between reduction and oxidation waves, cyclic voltammograms at 135°C were recorded at various expansions of the potential scan range up to -2.5V and 1.5V, respectively - started from the OCP in the cathodic direction. The resulting voltammograms can be seen in *Figure 4.10*.

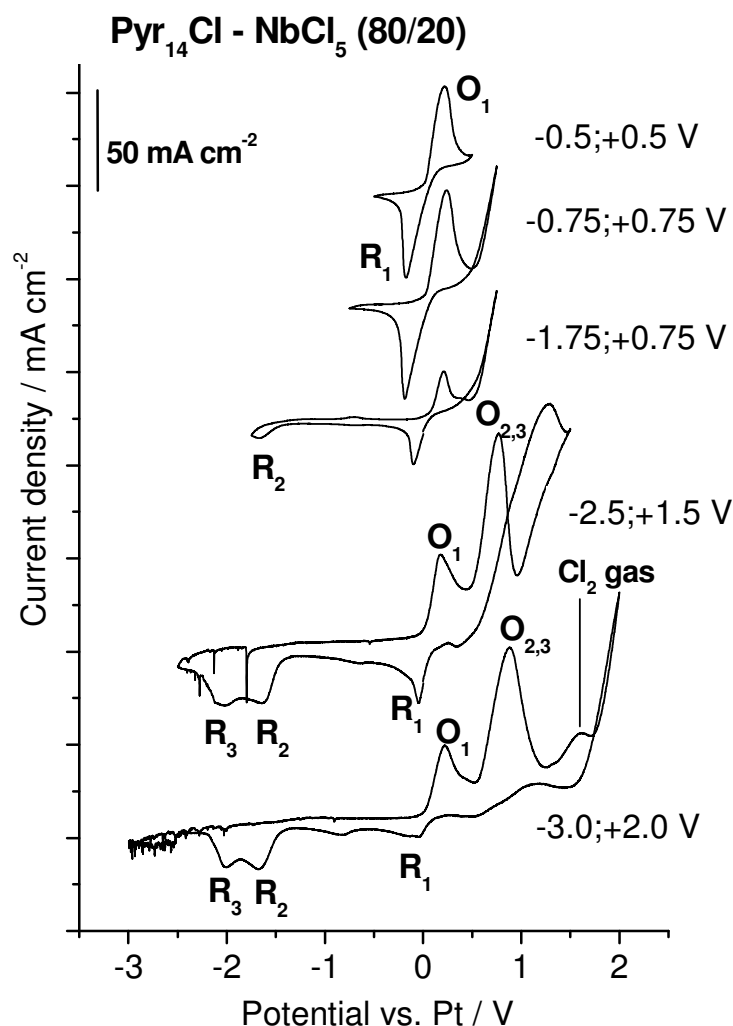


Figure 4.10. Cyclic voltammograms of $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ mixtures at $x=0.80$ recorded for different potential windows ($T=135^\circ\text{C}$; scan rate 100 mV s^{-1})

The cyclic voltammograms of $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.8$ demonstrate that the electrochemical reduction of niobium apparently proceeds in three steps (peaks R_1 , R_2 , R_3), which correlates with three oxidation peaks (from O_1 to O_3). For the first redox couple, R_1/O_1 the areas under the oxidation and reduction waves are comparable for the scan range -0.75V to 0.5V testifying the reversibility of this process. In the potential range -1.75V to 0.75V , the areas of the peaks R_1 and O_1 are still similar but the positions of the peaks has changed slightly. For the moment one it seems that the couple R_1/O_1 is still reversible in this range. When the scan range is further enlarged ($-2.5\text{V} \div 1.5\text{V}$), a reduction of the current density of R_1 occurs and further reduction waves R_2 and R_3 are apparent. Analogous to the observations made in high temperature molten salts, *e.g.* for $\text{NbCl}_5/\text{NaCl-CsCl}$ mixtures [185] we tentatively assign these waves to reductions of $\text{Nb(IV)} \rightarrow \text{Nb(III)}$ and $\text{Nb(III)} \rightarrow \text{Nb}$.

In order to test the electrochemical reversibility of the system, cyclic voltammograms were recorded at different scan rates (*Figure 4.11.*).

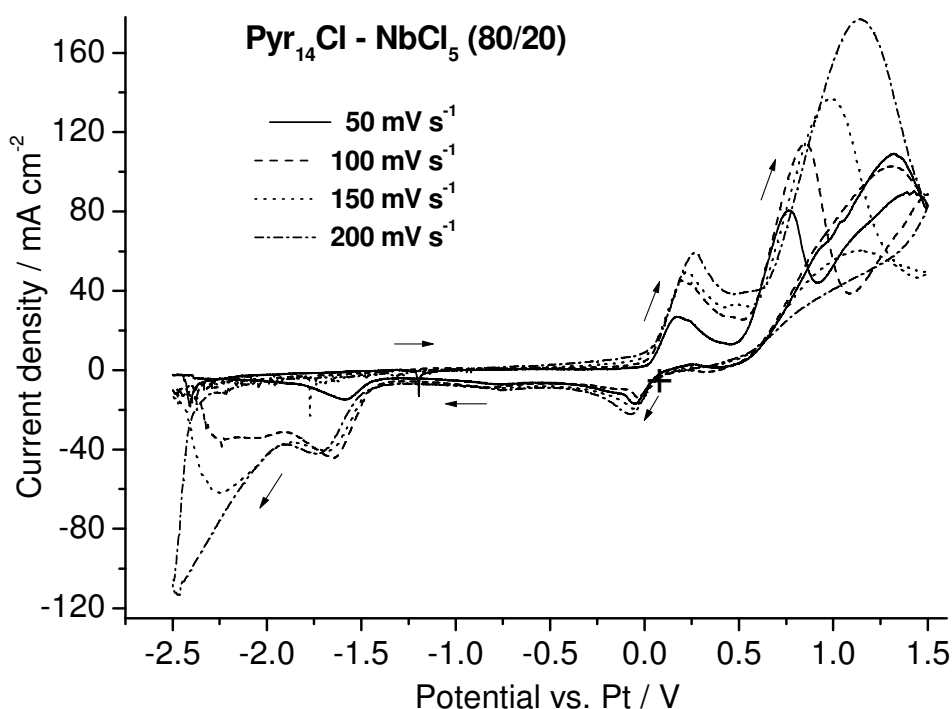


Figure 4.11. Cyclic voltammograms of the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ionic liquid at $x=0.80$ recorded at different scan rates ($T=135\text{-}140^\circ\text{C}$)

While the current densities of peak R_2 and especially that of R_3 clearly grow with increasing scan rate the intensity of R_1 remains nearly unaffected. One possible explanation is that higher aggregated species like niobium chloride clusters, Nb_3Cl_8 are formed but that cannot be detected by Raman spectroscopy. Due to the larger size and lower mobility of niobium chloride clusters, one can expect that at higher scan rates deviations from a simple diffusion controlled law may occur. On the other hand, adsorption kinetics may determine the deposition near the peak R_3 around -2.1 V.

In order to get insight into the reversibility of the redox process R_1/O_1 , it has been studied within narrow bounds from -0.5 V to 0.5 V at different scan rates (*Figure 4.12.*).

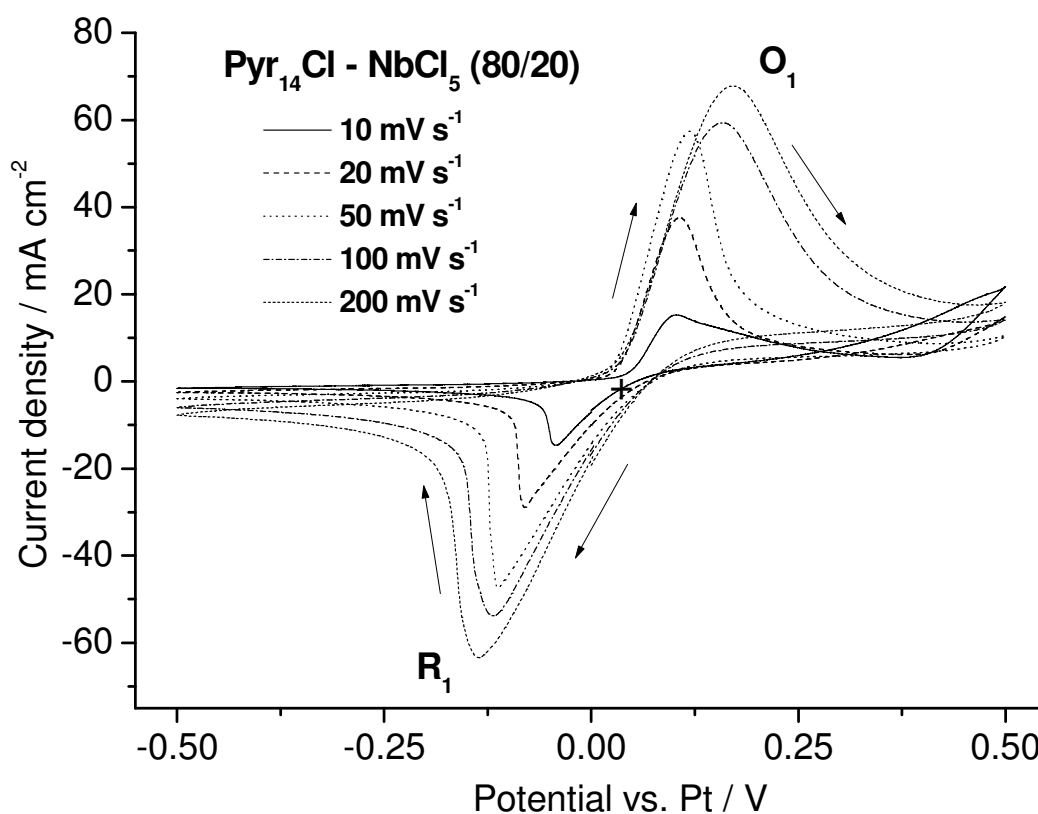


Figure 4.12. Cyclic voltammograms of the $(x)Pyr_{14}Cl-(1-x)NbCl_5$ ionic liquid at $x=0.80$ recorded at different scan rate for the first redox couple R_1/O_1 ($T=135-140^\circ C$)

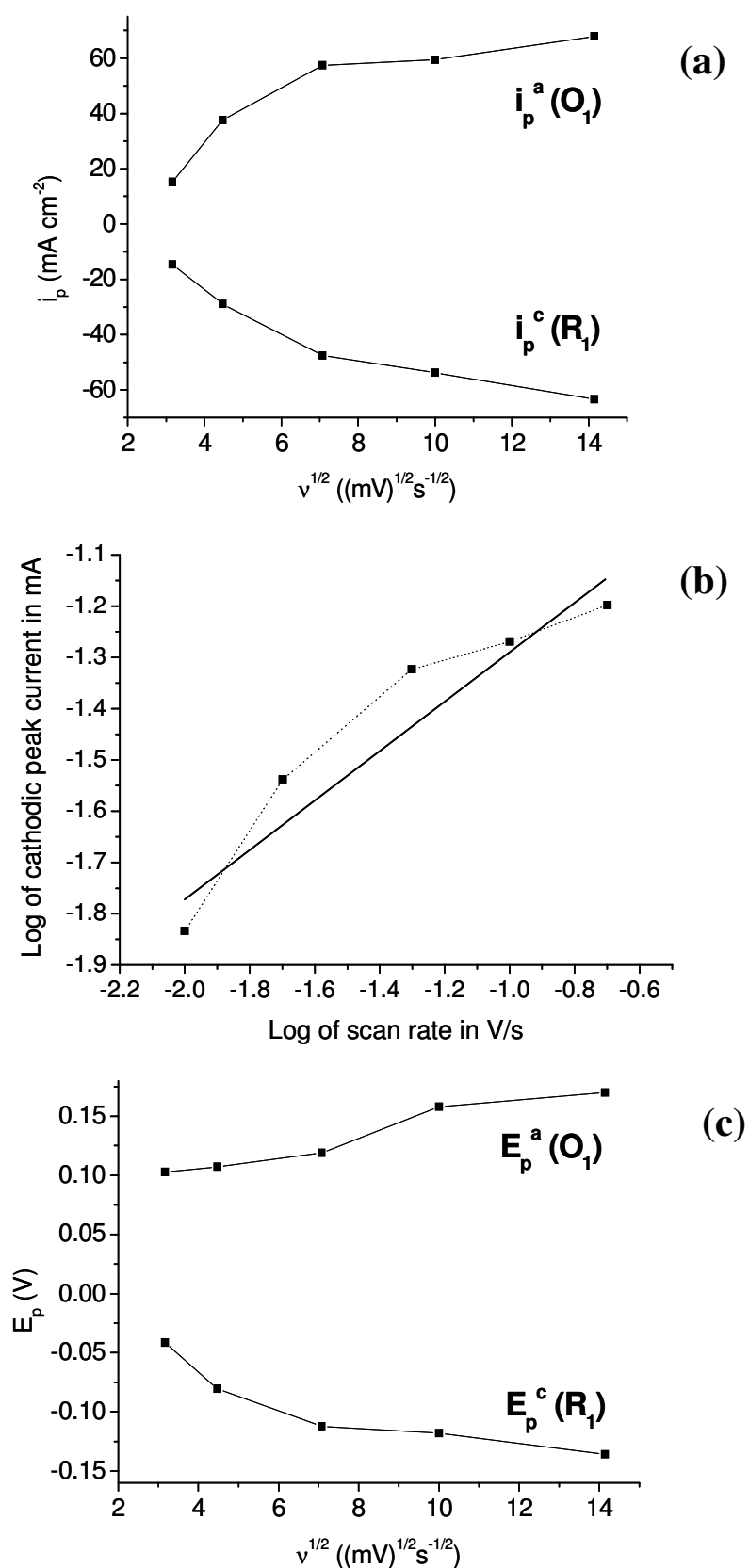


Figure 4.13. Correlation between the current densities (i_p) of the waves R_1 and O_1 and the square root of the scan rate ($v^{1/2}$) (a); plot of the log i_p cathodic versus log v (b), and correlation of peak potentials (E_p) of the waves R_1 and O_1 and the square root of the scan rate ($v^{1/2}$) (c)

The peak currents of both the reduction and oxidation peaks were proportional to the square root of the scan rate indicating the diffusion control (*Figure 4.13. a*). A plot of the log i_p cathodic versus log v was linear with slope of 0.5 typically for a diffusion peak (*Figure 4.13. b*). The peak potentials do not depend on the scan rate: the peak potential of the cathodic wave R_1 slightly shift to more negative values and the oxidation wave O_1 slightly move to the positive direction with increase of the scan rate (*Figure 4.13. c*).

In discussing these data in the light of general reversibility diagnostics of redox processes it must be taken into account that in the temperature range 135-140°C the temperature effect on the cyclic voltammograms is relatively large and so – with a temperature uncertainty of 10°C - a quantitative evaluation of the scan rate dependence of the cyclic voltammograms is made difficult.

In a first approximation the areas under the respective reduction and oxidation waves are equal and the corresponding peak currents increase with the square root of the scan rate v . This is indicative of a diffusion controlled reversible process. However, the peak separation clearly increases with v which is typically found in irreversible systems. So, a clear conclusion on the reversibility of the redox reaction cannot be drawn on the basis of these data.

Assuming a reversible reaction a value of ≈ 1 is estimated from the separation of the peak potentials for the number of transferred electrons. The number of electrons, n transferred in the electron reaction for reversible couple was calculated from the separation between the peak potentials [189]:

$$\Delta E_p = |E_p^a - E_p^c| = 2.2 RT/nF \quad (4.2.)$$

The results of these measurements and calculations are summarized in *Table 4.1*.

Table 4.1. Cyclic voltammetric data for the redox process of niobium(V) in the (x)Pyr₁₄Cl-(1-x)NbCl₅ mixture at x=0.80 (potential window -0.5 ÷ 0.5V). Potentials vs. Pt.

$v/$ [V s ⁻¹]	$v^{1/2}/$ [V ^{1/2} s ^{-1/2}]	$i_p^c(R)/[A\text{ cm}^{-2}]$	$i_p^a(O)/[A\text{ cm}^{-2}]$	PR	$E_p^c / [V]$	$E_p^a / [V]$	$E^0 / [V]$
0.01	0.10	-1.46×10^{-2}	1.529×10^{-2}	1.043	-0.041	0.103	0.031
0.02	0.14	-2.89×10^{-2}	3.755×10^{-2}	1.297	-0.081	0.107	0.013
0.05	0.22	-4.74×10^{-2}	5.743×10^{-2}	1.210	-0.112	0.119	0.004
0.10	0.32	-5.38×10^{-2}	5.936×10^{-2}	1.103	-0.118	0.158	0.040
0.20	0.45	-6.34×10^{-2}	6.783×10^{-2}	1.070	-0.136	0.170	0.017

Where, $E^0 = (E_p^a + E_p^c) / 2$ is called formal potential for a couple.

Peak current ratio $PR = |i_p^a / i_p^c|$

4.1.1.9. Cyclic voltammetry of basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.60

Cyclic voltammograms of ionic liquids at x=0.6 depending on the temperature are presented in *Figure 4.14*. The current density strongly increases as the temperature grows. The optimal temperature for electrochemical measurements again is found in the range 135-145°C.

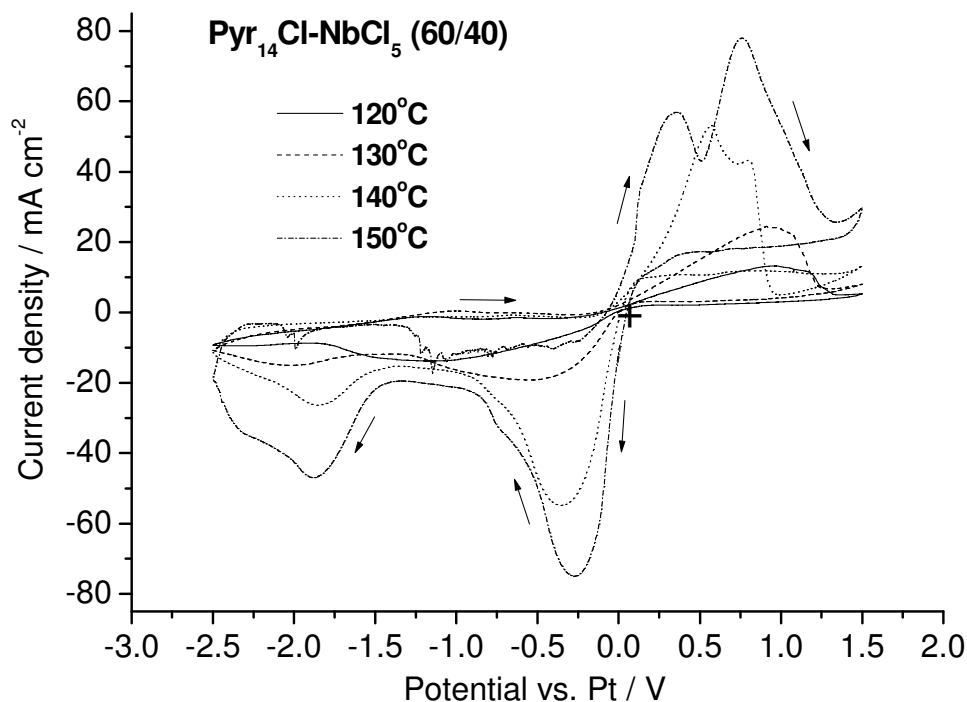


Figure 4.14. Cyclic voltammograms of the (x)Pyr₁₄Cl-(1-x)NbCl₅ ionic liquids at x=0.60 (WE-Pt disc; CE-GC; RE-Pt wire; scan rate 100 mV s⁻¹): temperature dependence

The correlation between reduction and oxidation peak potentials has been estimated on the basis of cyclic voltammograms at 140°C recorded with various expansions in the potential range up to -2.5V to 1.5V (starting from the OCP in the cathodic direction) (*Figure 4.15*).

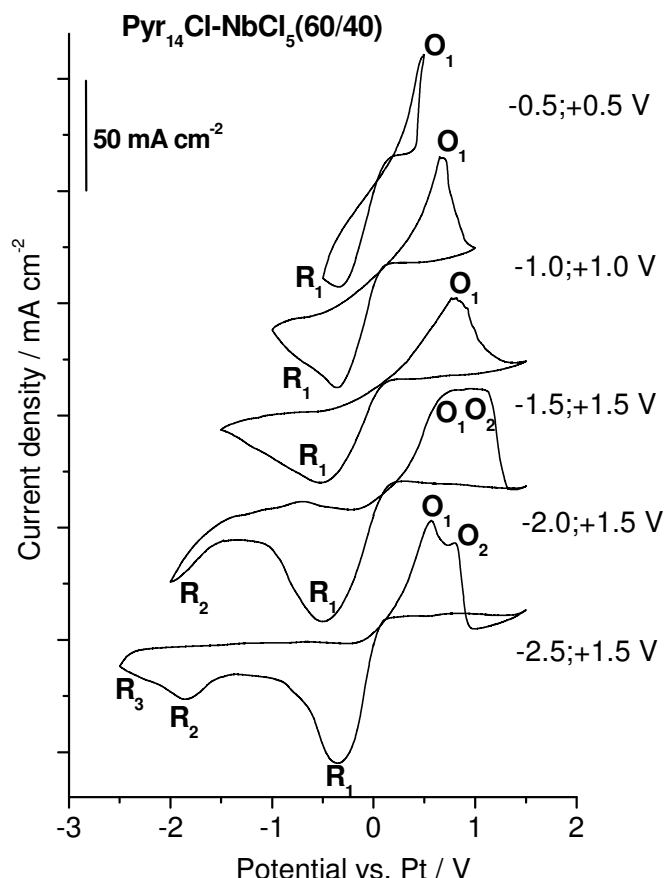


Figure 4.15. Cyclic voltammograms of the (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures at x=0.60 recorded for different potential windows (T=140°C; scan rate 100 mV s⁻¹)

The CV recorded from -2.5 to 1.5V exhibits two clear reduction waves R₁, R₂ and a third R₃ is indicated. The corresponding oxidation waves are marked by O₁ and O₂. According to the Raman spectra, the ionic liquid at x=0.60 is dominated by the octahedral NbCl₆⁻ (Nb⁵⁺) complexes. Therefore the first major reduction peak R₁ at -0.4 V is due to the reduction of Nb⁵⁺ → Nb⁴⁺. The area of this peak is significantly higher in comparison with that of the composition x=0.80 (Figure 4.7.) which is in agreement with a higher concentration of Nb⁵⁺ ions in the x=0.60 melts. In the potential range between -1.5V and 1.5V, the areas under the reduction wave R₁ and the oxidation wave O₁ are comparable in magnitude. The reduction peaks at -1.9V (R₂) and that indicated at -2.4V (R₃) presumably are due to the further reduction of Nb⁴⁺ species to lower oxidation states.

4.1.1.10. Cyclic voltammetry of the acidic ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.40$

The behaviour of observed reduction and oxidation peaks in the cyclic voltammograms remains the same as the temperature grows (*Figure 4.16.*). Temperature mainly influences the magnitude of the current densities of the redox peaks. Comparing with basic ionic liquids, the resulting current densities are higher at $x=0.40$. The optimal temperatures for electrochemical measurements again are found in the range 135-145°C.

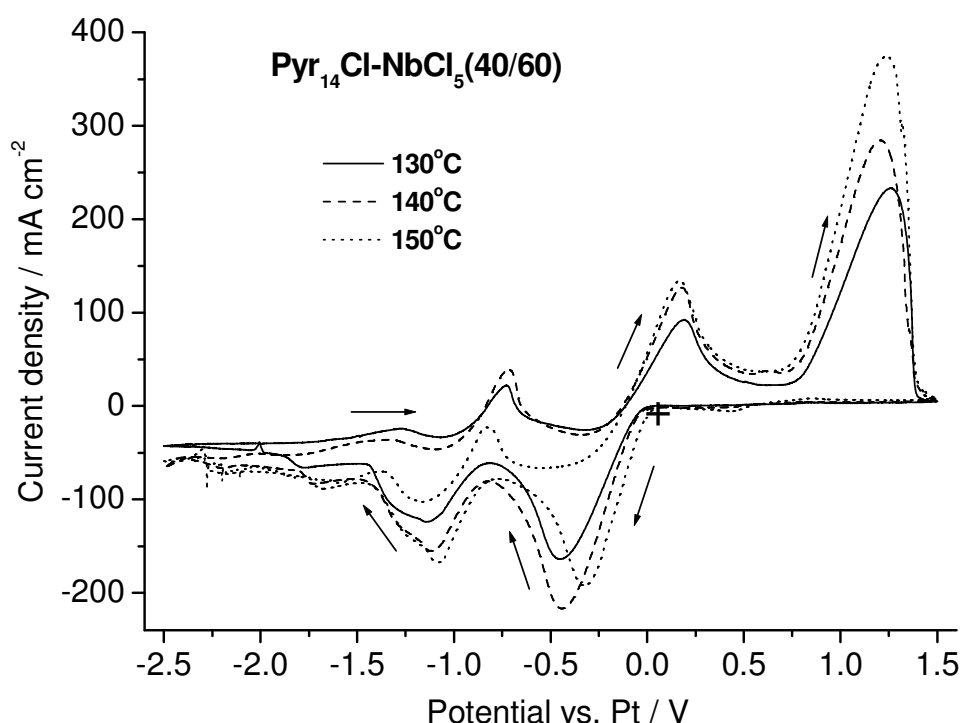


Figure 4.16. Cyclic voltammograms of the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ionic liquids at $x=0.40$ (WE-Pt disc; CE-GC; RE-Pt wire; scan rate 100 mV s^{-1}): temperature dependence

Cyclic voltammograms at $x=0.40$ recorded between different potential windows are presented in *Figure 4.17*. Many of the features of the redox couple R_1/O_1 such as the comparable size of the areas under the reduction and oxidation waves or the constant peak potentials indicate a reversible process.

The widening of the potential range ($-1.5 \text{ V} \div 0.75 \text{ V}$) clearly demonstrates the appearance of a second redox couple, R_2/O_2 whereby the oxidation peak O_2 is observed at a more negative potential (-0.70 V) than O_1 (0.21 V). Further widening of the potential range up to $-1.5 \text{ V} \div 1.5 \text{ V}$ leads to the appearance of an additional oxidation peak, O_3 (1.23 V) which does not have a corresponding reduction peak in this potential range. One can assign this oxidation peak to Cl_2 gas evolution. With excess of NbCl_5 , the electrochemical active species differ significantly from those determined in basic ionic liquids (*Figure 4.7.*). This is apparent in the characteristic differences of the respective cyclic voltammograms.

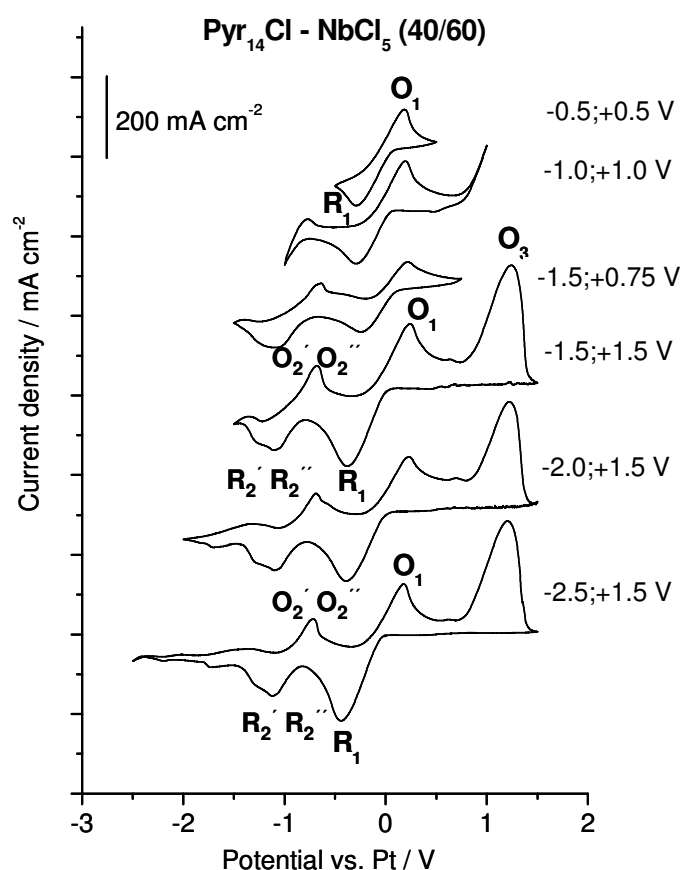
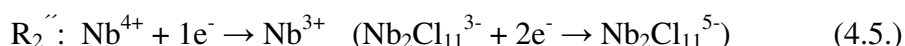
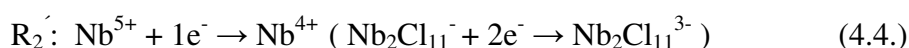
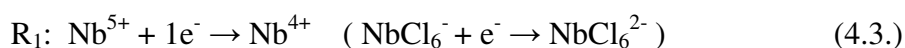


Figure 4.17. Cyclic voltammograms of liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ mixtures at $x=0.40$ recorded between different potential windows ($T=140^\circ\text{C}$; scan rate 100 mV s^{-1})

As two species of Nb^{5+} , namely the dominant NbCl_6^- octahedra and minor amount of binuclear $\text{Nb}_2\text{Cl}_{11}^-$ complexes have been identified in the Raman spectra of acidic melts at operating temperatures, it is reasonable to assume that the electrochemical reduction of niobium(V) is limited by a one electron transfer at -0.45 V (R_1) for NbCl_6^- (Equation 4.3.).

The further reduction of NbCl_6^{2-} species would be expected at -1.9 V that was established for basic composition at $x=0.60$. Instead of that, the next reduction peaks, R_2' and R_2'' were observed at more positive potentials and they can be assigned to the transfer of two electrons for $\text{Nb}_2\text{Cl}_{11}^-$ at -1.12 V (R_2') and -1.27 V (R_2''), respectively (Equations 4.4., 4.5.). This assignment implies that in the acidic ionic liquids only the reduction of niobium(V) to niobium(III) can be achieved leads to the following scheme:



In concluding this section a summary of the characteristic peak potential values of the relevant redox reactions in both basic and acidic (x)Pyr₁₄Cl – (1-x)NbCl₅ ionic liquids is given in Table 4.2.

Table 4.2. Characteristic peak potentials of redox reactions in basic ($x=0.80$ and $x=0.60$) and acidic ($x=0.40$) ionic liquids (x)Pyr₁₄Cl – (1-x)NbCl₅ recorded versus Pt-quasi reference electrode at 140°C

Basic ionic liquid $x=0.80$		Basic ionic liquid $x=0.60$		Acidic ionic liquid $x=0.40$	
Peak	Potential (V)	Peak	Potential (V)	Peak	Potential (V)
R_1	-0.02	R_1	-0.40	R_1	-0.45
R_2	-1.70	R_2	-1.90	R_2'	-1.12
R_3	-2.10	R_3	-2.40	R_2''	-1.27
O_1	+0.20	O_1	+0.50	O_1	+0.21
$O_{2,3}$	+0.87	O_2	+0.80	O_2', O_2''	-0.70
Cl_2 gas	+1.50			O_3	+1.23
				(Cl_2 gas)	

4.1.1.11. Conclusions

The combination of Raman spectroscopic measurements with electrochemical studies for the first time enabled a relatively detailed picture of the electrochemical reduction of NbCl_5 in the ionic liquid electrolyte 1-butyl-1-methylpyrrolidinium chloride. The optimum temperature range for this reduction is found to be rather limited (135-145 °C) due to the high viscosity of the ionic liquid at lower temperatures and its starting decomposition at elevated temperatures.

In the basic melts the dominating electrochemical active species are NbCl_6^{2-} complexes as shown by the Raman spectra. Presumably they can be reduced to metallic niobium in two steps:



In acidic melts NbCl_6^- and $\text{Nb}_2\text{Cl}_{11}^-$ species coexist and the electrochemical reduction mechanism now is:

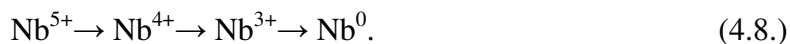


These results are summarized in *Table 4.3*. Although we did not succeed to characterize metallic niobium deposits with these ionic liquids the main issue of this study was to elucidate the reduction mechanism which finally may lead to niobium deposition.

Table 4.3. Main electrochemical reduction mechanisms of NbCl₅ in different ionic liquids as determined from combined Raman and electrochemical measurements

Ionic liquid (x)Pyr ₁₄ Cl- (1-x) NbCl ₅	Predominant form of niobium(V) chloride complexes (Raman spectroscopy)	Tentative scheme of electrochemical reduction
Basic ionic liquid x=0.80	<i>Solid sample, 20°C</i> NbCl₆⁻ (O_h) (Nb⁵⁺) (70%) NbCl₆²⁻ (O_h) (Nb⁴⁺) (30%) <i>Liquid sample, 140°C</i> NbCl₆⁻ (O_h) (Nb⁵⁺) (25%) NbCl₆²⁻ (O_h) (Nb⁴⁺) (75%)	<u>135-145°C</u> -0.02 V: one electron transfer of minor species NbCl₆⁻ $\text{Nb}^{5+} + 1\text{e}^- \rightarrow \text{Nb}^{4+}$ - in the potential range -0.5V ÷ 0.5V -1.70 V: one electron transfer of the main species NbCl₆²⁻ $\text{Nb}^{4+} + \text{e}^- \rightarrow \text{Nb}^{3+}$ -2.10 V: further reduction of Nb³⁺ to metallic niobium is possible
Basic ionic liquid x=0.60	<i>Solid sample, 20°C</i> NbCl₆⁻ (O_h) <i>Liquid sample, 140°C</i> NbCl₆⁻ (O_h) dominant species	<u>135-145°C</u> -0.40 V: reduction of dominant NbCl₆⁻ species $\text{Nb}^{5+} + 1\text{e}^- \rightarrow \text{Nb}^{4+}$ -1.90 V and -2.40 V: reduction of Nb⁴⁺ species to lower oxidation states
Acidic ionic liquid x=0.40	<i>Solid sample, 20°C</i> Nb₂Cl₁₀ dominant species <i>Liquid sample, 140°C</i> NbCl₆⁻ (50 %) Nb₂Cl₁₁⁻ (50 %)	<u>135-145°C</u> -0.45 V: one electron transfer of NbCl₆⁻ species $\text{Nb}^{5+} + 1\text{e}^- \rightarrow \text{Nb}^{4+}$ (NbCl₆⁻ + 1e⁻ → NbCl₆²⁻) -1.12 V and -1.27 V: two electrons transfer of Nb₂Cl₁₁⁻ species $\text{Nb}^{5+} + 1\text{e}^- \rightarrow \text{Nb}^{4+}$ (Nb₂Cl₁₁⁻ + 2e⁻ → Nb₂Cl₁₁³⁻) $\text{Nb}^{4+} + 1\text{e}^- \rightarrow \text{Nb}^{3+}$ (Nb₂Cl₁₁³⁻ + 2e⁻ → Nb₂Cl₁₁⁵⁻) Only the reduction of niobium(V) to niobium(III) can be achieved

Comparing these observations with findings obtained for high temperature molten salts, several similarities can be stated. In fused alkali metal solvents with added NbCl_5 , the equilibrium between NbCl_6^- and NbCl_6^{2-} octahedral species prevails [182]. From high temperature impedance measurements evidence [185] is found for a three step reduction mechanism according to:



It is also interesting to note that very similar reactions have been observed for the electrochemical reduction of the refractory metal compound TaCl_5 in alkali metal chloride melts at high temperatures and, more recently, in basic pyrrolidinium based ionic liquids [148]. One may conclude - at least from the electrochemical point of view of refractory metal ions reduction - that high temperature molten salts and ionic liquids may be considered as “two sides of the same coin”.

4.1.2. Spectroscopic and electrochemical studies of ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ using various systems with niobium electrode

4.1.2.1. Introduction

This chapter presents the results on the study of electrochemical behaviour of niobium(V) in ionic liquids (x)1-butyl-1-methylpyrrolidinium chloride-(1-x)NbCl₅ with various electrodes in combination with Raman spectroscopic data. The formation of niobium species in different oxidation states was confirmed by means of Raman spectroscopy.

The anodic dissolution of niobium was investigated in the most explored system: the basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80. To study the niobium electrode behaviour in contrast to standard platinum electrode in this ionic liquid, the anodic curves were recorded using both of them at the same conditions. Three electrodes scheme: Nb or Pt as a working electrode, Pt as a counter one and a Pt wire as a quasi-reference, was applied for electrochemical investigations.

Chemical and electrochemical dissolution of niobium in ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 and 0.60 was investigated by means of electrochemical methods in combination with Raman spectroscopic studies at operating temperatures. The chemical dissolution of niobium was investigated when niobium powder was added to the electrolyte. The electrochemical dissolution was achieved by using of niobium metal rod as a consumable anode in the contract to the stable glassy carbon anode (Pt as a working electrode, Nb rod as a counter one and a Pt wire as a quasi-reference electrode) during chronoamperometric and cyclic voltammetric measurements. Special attention was paid to the investigation of the reduction mechanism of niobium(V) in the melt considering the presence of the ions in different oxidation state.

4.1.2.2. Anodic dissolution of niobium in basic ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.80$

The study of the anodic behaviour of niobium electrode can provide the useful information about the nature of the intermediates which are the products of the interaction between the metal and the components of electrolyte. The anodic dissolution of niobium metal electrode was carried out in basic ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ($x=0.80$) at the optimal temperature 140°C using three electrode setup: Nb rod (diameter 1mm) as a working electrode, Pt as a counter one and a Pt wire as a quasi-reference electrode. The anodic curves of Nb electrode in different portions of the same electrolyte are presented in *Figure 4.18*.

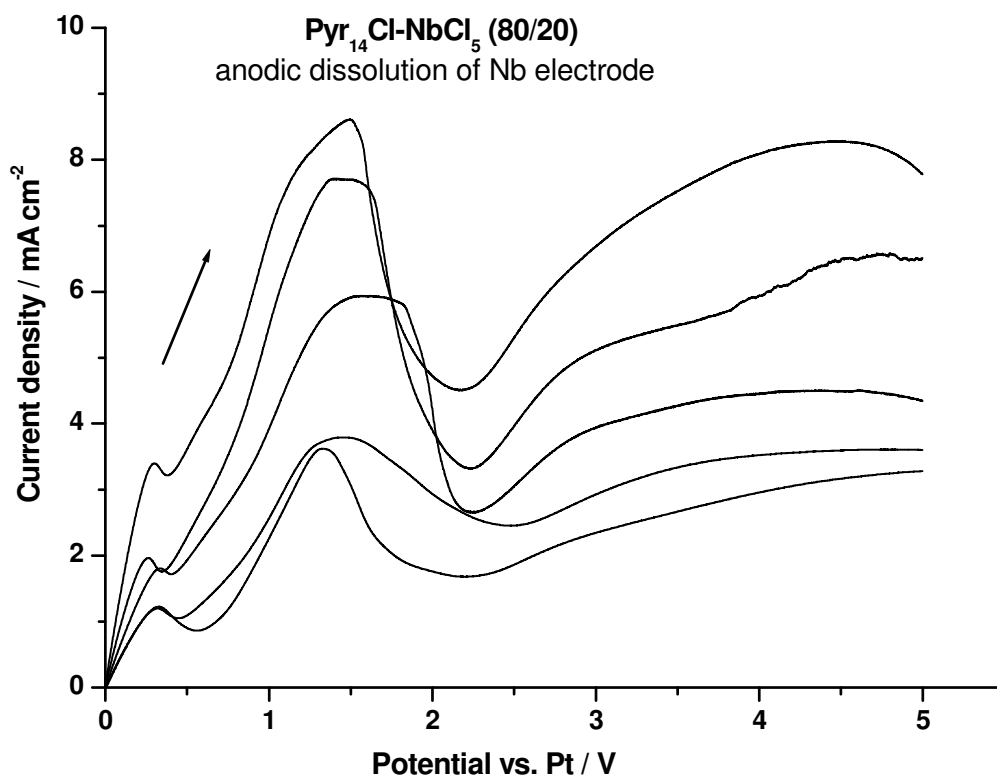


Figure 4.18. Anodic curves of Nb electrode in different portions of the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ($x=0.80$) ($T=140^\circ\text{C}$; scan rate 100 mV s^{-1})

The analysis of the obtained anodic curves demonstrates that niobium has an active dissolution region at the potentials from 1.5 V to 1.7 V followed by the second activation region after a short passive state.

To determine the amount of matter transformed during the electrolysis reaction ($M^0 \rightarrow M^{n+} + ne^-$), the coulometry on niobium electrode has been performed. For that purpose, the weight of the niobium electrode was carefully measured before and after each experiment. However, one should note that the weight loss was small because of the small size of the electrode (0.471cm^2) and the amount of electrolyte (0.5 ml). Nevertheless, the value of n can be determined from the weight-loss measurements using *Equation 4.9.*:

$$n = I \tau M / \Delta W F \quad \text{or} \quad n = Q M / \Delta W F, \quad (4.9.)$$

where n is the apparent dissolution valence, I is the current in amperes, τ is the dissolution time in seconds, Q is the electric charge in coulombs ($C=A \text{ s}$), M is the molecular weight of the dissolved material in g/mole, ΔW is the anodic weight loss in grams and F is the Faraday constant in $A \text{ s mole}^{-1}$. The sequence of the current passed through the system and the calculated valence of niobium dissolved are collected in *Table 4.4.*

Table 4.4. The sequence of the current passed through the electrolyte $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ($x=0.80$) and the calculated valence of niobium dissolved

Time τ, s	Current I, A	Valence of Nb dissolved n
300	0.24×10^{-4}	0.06
900	0.28×10^{-4}	0.24
3600	0.54×10^{-4}	1.87
7200	0.53×10^{-4}	3.26

4.1.2.3. Cyclic voltammetry in basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 using niobium soluble electrode

To explain the role of Nb soluble electrode in the mechanism of electrochemical reduction of niobium(V) in details, three additional experiments were performed. Three portions of the ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 were synthesized and the cyclic voltammograms were recorded using three different set of electrodes:

- (1) cyclic voltammograms of the first portion of electrolyte were recorded using standard three-electrode setup: Pt disk as the working electrode and the glassy carbon (GC) as the counter electrode versus Pt wire quasi-reference one(Pt/GC/Pt) (*Figure 4.19., solid curve*);
- (2) in the second portion, niobium wire was used instead of the glassy carbon as the counter electrode (Pt/Nb/Pt) (*Figure 4.19., dash curve*);
- (3) in the third mixture, niobium was primarily dissolved electrochemically using chronoamperometric technique, than cyclic voltammograms were recorded using Pt/GC/Pt electrode system as in the first case (*Figure 4.19., dot curve*).

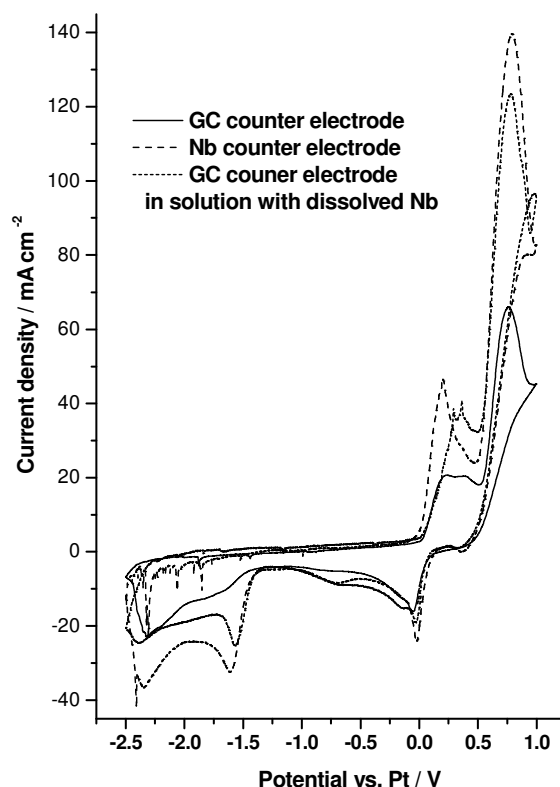


Figure 4.19. Cyclic voltammograms of the (x)Pyr₁₄Cl-(1-x)NbCl₅ mixture at x=0.8: *solid curve* – GC counter electrode, *dash curve* – Nb counter electrode, *dot curve* – GC counter electrode in solution with dissolved Nb (T=140°C; scan rate 100 mV s⁻¹)

(1) - The mechanism of electrochemical reduction of niobium(V) in basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 using Pt/GC/Pt electrode system (GC as counter electrode) was already discussed in details (*section 4.1.1.8.*). A three step reduction mechanism according to the scheme: $\text{Nb}^{5+} \rightarrow \text{Nb}^{4+} \rightarrow \text{Nb}^{3+} \rightarrow \text{Nb}^0$ at potentials -0.02 V, -1.70 V and above -2.10 V vs. Pt reference electrode, respectively was proposed.

(2) - The cyclic voltammogram of ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 using niobium wire as the counter electrode shows that additional amount of niobium ions leads to the increase of the current density and intensity of reduction and oxidation peaks (*Figure 4.19., dash curve*). An additional reduction peak appears at -0.75 V. This could designate that extra amount of niobium(V) species change the equilibrium $\text{Nb(V)} \leftrightarrow \text{Nb(IV)}$ ions in the solution. Consequently, the reduction mechanism of niobium(V) in the mixture is changed.

(3) - The cyclic voltammogram of ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 using GC counter electrode in the solution where Nb was primarily dissolved electrochemically (*Figure 4.19., dot curve*) shows that the reduction process is almost the same as with Nb counter electrode (anode). The reasonable explanation could be that in both cases the electrolyte was saturated with niobium ions and it makes no difference in which way: via the Nb soluble electrode or via Nb, primarily dissolved electrochemically. One can also mention that the content of chlorine ions, Cl⁻ in the electrolyte at x=0.80 is enough to react with Nb ions, which are coming from the soluble anode or electrochemical dissolution of niobium. In this case the reduction mechanism of niobium(V) becomes more complicated.

4.1.2.4. Raman spectroscopy of basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 using niobium soluble electrode

The Raman spectra of ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 were recorded after chronoamperometry (CA) performed with Pt and Nb soluble electrodes. The electrochemical measurements were conducted at optimal temperature 140°C; the duration of CA was 5 min., 15 min., 1 hour, and 2 hours. (Figure 4.20). The optimal parameters for CA were found on the base of cyclic voltammograms and anodic curves (active dissolution region). To clarify the role of the Nb electrode contrary to the Pt electrode in reduction process, both of them were used as working electrodes with equal effective area under the same conditions.

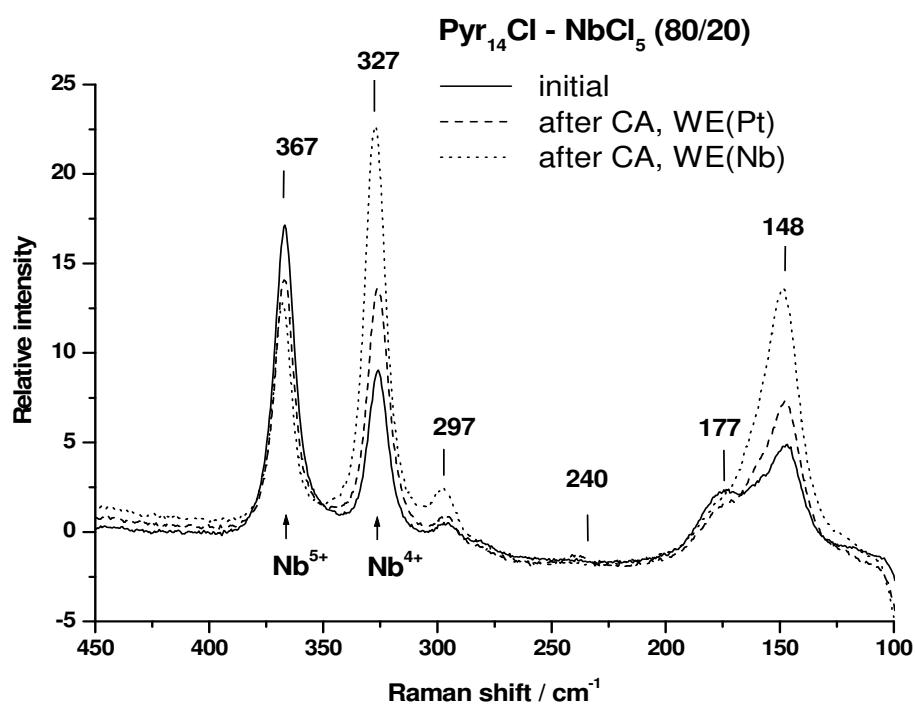


Figure 4.20. Raman spectra of the quenched (x)Pyr₁₄Cl-(1-x)NbCl₅ mixture at x=80 before (solid line) and after CA (duration 1 hour) with Pt (dash line) and Nb (dot line) electrodes

The Raman spectra of the basic mixture at x=0.80 exhibit vibrations at 177 cm⁻¹, 297 cm⁻¹, and 367 cm⁻¹ which are the characteristic bands for the octahedral complex NbCl₆⁻ (Nb⁵⁺). The bands observed at 148 cm⁻¹ and 327 cm⁻¹ are assigned to the octahedral species NbCl₆²⁻ (Nb⁴⁺). After CA performed with Pt electrode, the intensity of the vibrations of the NbCl₆²⁻ (Nb⁴⁺) species increases demonstrating the accumulation of Nb(IV) valence state. The

using of the Nb soluble electrode leads to the further increase of the amount of Nb(IV) species in the electrolyte.

The Raman data support the changes observed in the cyclic voltammograms in *Figure 4.21*, namely that the shift of equilibrium $\text{Nb(V)} \leftrightarrow \text{Nb(IV)}$ towards Nb(IV) species in basic ionic liquid at $x=0.80$ influences the mechanism of electrochemical reduction. It became more complicated since different electrochemically active species are present in electrolyte. This confirms also the mentioned above transfer of ions from metal niobium electrode to solution during electrolysis.

4.1.2.5. Raman spectroscopy of ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 and x=0.60 with different source of niobium ions

The spectroscopic and electrochemical experiments were performed in ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at x=0.80 and 0.60 with the additive of Nb powder and with electrochemical niobium dissolution.

Raman spectroscopy was used to obtain the information about the complexes of niobium in different oxidation states in ionic liquids at x=0.80 and 0.60 which were formed due to the introducing of Nb powder and using of the niobium soluble electrode. The corresponding Raman spectra are presented in *Figure 4.21*. The observed vibrational frequencies of niobium species in the (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures at x=0.80 and 0.60 are collected in *Table 4.5*.

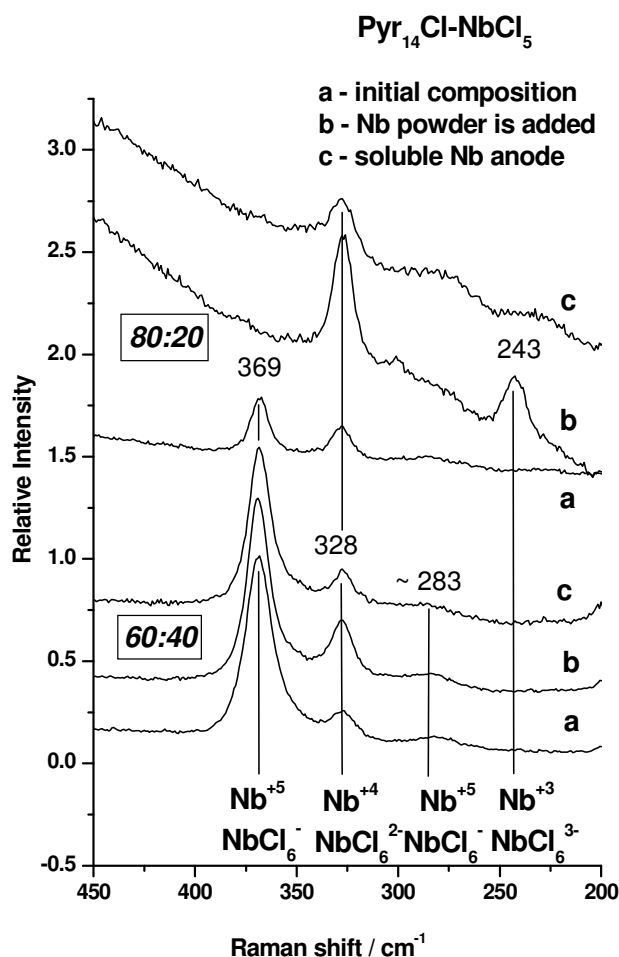


Figure 4.21. Raman spectra of the (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures (x=0.80 and x=0.60): (a) – initial ionic liquids; (b) – with the additive of Nb powder; (c) – with Nb soluble electrode

Table 4.5. The observed vibrational frequencies of niobium species in the (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures at x=0.80 and x=0.60 with the additive of Nb powder and with Nb soluble electrode

Mixture	Initial composition	Nb powder is added	Soluble Nb electrode	Complex
80/20	369 s	-	-	NbCl ₆ ⁻
	328 m	328 s	328 s	NbCl ₆ ²⁻
	283 vw	-	-	NbCl ₆ ⁻
	-	243 s	-	NbCl ₆ ³⁻
60/40	369 s	369 s	369 s	NbCl ₆ ⁻
	328 m	328 m	328 m	NbCl ₆ ²⁻
	283 vw	283 vw	283 vw	NbCl ₆ ⁻

According to the Raman data, the initial ionic liquid at $x=0.80$ consists of the mixture of niobium(V) and niobium(IV) species. The additive of Nb powder leads to the reduction of niobium(V) species with the formation of niobium(IV), NbCl₆²⁻ (328 cm⁻¹) and presumably niobium(III), NbCl₆³⁻ (243 cm⁻¹) species. The vibration of NbCl₆⁻ species at 369 cm⁻¹ does not observed anymore in the Raman spectrum. When niobium soluble electrode was used as an additional source of niobium ions in the electrolyte, only niobium(IV) species, NbCl₆²⁻ (328 cm⁻¹) were identified in the electrolyte.

The Raman spectrum of the initial mixture at $x=0.60$ demonstrates that the dominant species are NbCl₆⁻ octahedra with a small amount of NbCl₆²⁻ complexes. The addition of Nb powder and the electrochemical dissolution of niobium do not cause the reduction of niobium(V) species and the Raman spectra of the ionic liquid as well as the ratio between NbCl₆⁻ and NbCl₆²⁻ complexes remain unchanged. (*Figure 4.21.*) .

4.1.2.6. Cyclic voltammetry of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.80$, $x=0.67$, and $x=0.60$ with different source of niobium ions

The corresponding cyclic voltammograms of the mixtures $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.80$, 0.67 and 0.60 recorded with glassy carbon and niobium counter electrodes are presented in *Figure 4.22*.

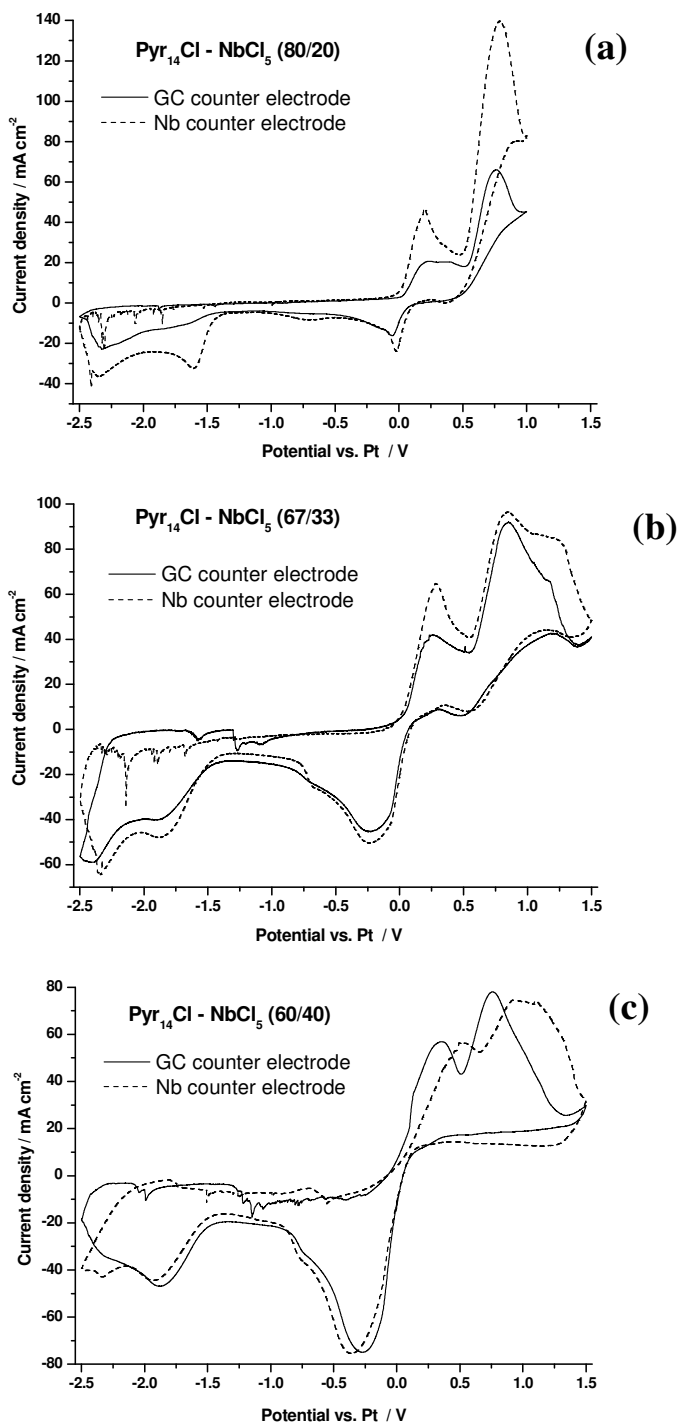
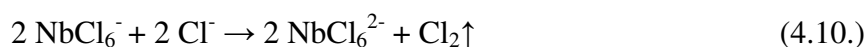


Figure 4.22. Cyclic voltammograms of the basic ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at different molar ratios: (a) $x=0.80$; (b) $x=0.67$, and (c) $x=0.60$ recorded with glassy carbon (solid curve) and niobium (dash curve) counter electrodes

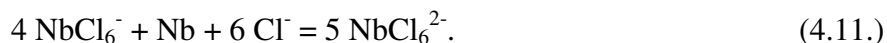
The mechanism of electrochemical reduction with niobium counter electrode in (x)Pyr₁₄Cl-(1-x)NbCl₅ mixture at x=0.80 differs significantly comparing with that one with the glassy carbon electrode: an additional peak appears at -0.75 V and the area of the reduction peak at -1.7 V increases significantly. According to the Raman data, the starting electrolyte contains a mixture of Nb(V) and Nb(IV) species. When niobium was dissolved electrochemically, only Nb(IV) species were identified in the electrolyte.

It was shown above (*section 4.1.1.8.*) that in the initial mixture at x=0.80 the self-reduction reaction:



takes place leading to the equilibrium between NbCl₆⁻ and NbCl₆²⁻ species.

When niobium is introduced to this system via soluble niobium anode, the further reduction of Nb(V) to Nb(IV) occurs:



In this case the cyclic voltammogram (*Figure 4.22.*, *dash curve* for 80/20) reflects the reduction of Nb(IV) as the dominant species.

The replacement of the glassy carbon electrode with niobium counter one does not cause the significant changes of the reduction processes in the (x)Pyr₁₄Cl-(1-x)NbCl₅ ionic liquids at x=0.67 and x=0.60 (*Figure 4.22.*, *b*) and *c*). Only small shifts of the peak potentials towards the cathodic direction are observed. The same niobium species, NbCl₆⁻ (dominant) and NbCl₆²⁻ for both mixtures were identified using Raman spectroscopy (*Table 4.5.*). One can suggest that at the ratio between Pyr₁₄Cl and NbCl₅ close or equal to 3:2 (x=0.67 and x=0.60), the quantity of free Cl⁻ anions is not enough to change the reduction mechanism of niobium(V). As a result the soluble niobium anode in these electrolytes serves only as a current conductor.

The overlapping of the cyclic voltammograms of the basic ionic liquids at $x=0.80$, 0.67, and 0.60 with the niobium counter electrode is presented in *Figure 4.23*.

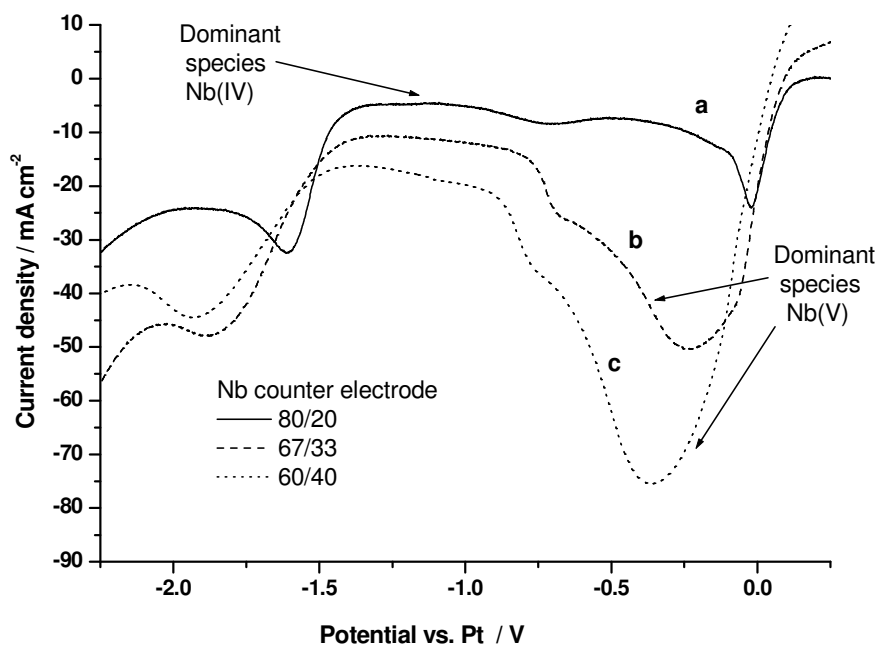


Figure 4.23. Cyclic voltammograms of the basic ionic liquids at $x=0.80$ (a), $x=0.67$ (b), and $x=0.60$ (c) with niobium counter electrode

The first reduction peak at -0.02 V in the cyclic voltammogram of the ionic liquid at $x=0.80$ (solid curve, a)) can be assigned to the reduction of the negligible amount of Nb(V) to Nb(IV) followed by the further reduction of the dominant Nb(IV) species.

So far as Nb(V) species are the dominant at $x=0.67$ and $x=0.60$, it is reasonable to assign the reduction peaks at potentials from -0.30 V to -0.36 V to the electron transfer $\text{Nb(V)} \rightarrow \text{Nb(IV)}$ and the reduction peaks at the potentials from -0.68 V to -0.78 V to the reduction $\text{Nb(IV)} \rightarrow \text{Nb(III)}$. The waves between -1.60 V and -1.95 V can be due to the further reduction of Nb(III).

4.1.2.7. Conclusions

Electrochemical behaviour of niobium(V) in the ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at various molar ratios with the additive of Nb powder and via Nb soluble electrode was investigated in details. The Raman spectroscopic data confirm the formation of niobium species in lower oxidation states.

The electrolyte at $x=0.80$ where Nb(V) and Nb(IV) species were identified by means of Raman spectroscopy and the self-reduction $\text{Nb(V)} \rightarrow \text{Nb(IV)}$ was confirmed earlier, demonstrates the shift of this equilibrium towards the formation of the Nb(IV) complexes when Nb soluble electrode was used.

In the electrolyte at $x=0.60$ where Nb(V) species are the dominant ones, the using of Nb soluble electrode does not cause the further reduction $\text{Nb(V)} \rightarrow \text{Nb(IV)}$ and does not lead to the accumulation of the Nb(IV) complexes. The mechanism of the electrochemical reduction of Nb(V) species in this electrolyte remains unchanged when Nb soluble electrode was used.

According to the common experience in high temperature molten salts electrolytes, the mean valence of niobium should be ~ 4.2 to promote the electrochemical deposition of niobium. Taking into account this observation, in ionic liquids the Nb soluble electrode can be applied to keep the niobium(IV) ions at the constant level during electroplating processes.

The ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at $x=0.80$ was considered as the most preferable for the electrochemical deposition of metallic niobium.

4.1.3. Electrochemical studies with the additives of alkali metal halides

4.1.3.1. Introduction

From the literature data on high temperature molten salts, it was found that the addition of alkali metal fluorides to molten salts electrolytes facilitates the electrodeposition of refractory metals such as tantalum. The effect of addition of LiF to the ionic liquid 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethylsulfonyl)imide containing TaF₅ used for electrodeposition of tantalum was investigated by S.Z. El Abedin *et al* [93, 94]. By addition of LiF to the electrolyte, the quality and the adherence of the electrodeposit were found to be improved. Although the role of LiF was not completely clear, the authors suggested that may be its effect is due to the ionic polarizability of Li⁺, resulting in a weakening of the Ta-F bonds, leading to a facilitation of tantalum deposition.

In present section we have investigated the influence of alkali metal halides, namely KF, RbF and CsF on the reduction of niobium(V) in ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at various molar ratios for the sake of electrodeposition of niobium. The study was carried out using cyclic voltammetry and chronoamperometry measurements complemented by ESEM/EDAX investigations.

4.1.3.2. Cyclic voltammetry of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ with the additives of alkali metal halides

The alkali fluorides KF (in amount of 5 and 10 mole %), RbF (5, 10, and 15 mole %), and CsF (5 and 10 mole %) were added to the ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ at the initial composition of $x=0.67$ and corresponding cyclic voltammograms are presented in Figures 4.24. – 4.26.

4.1.3.2.1. Additives of KF

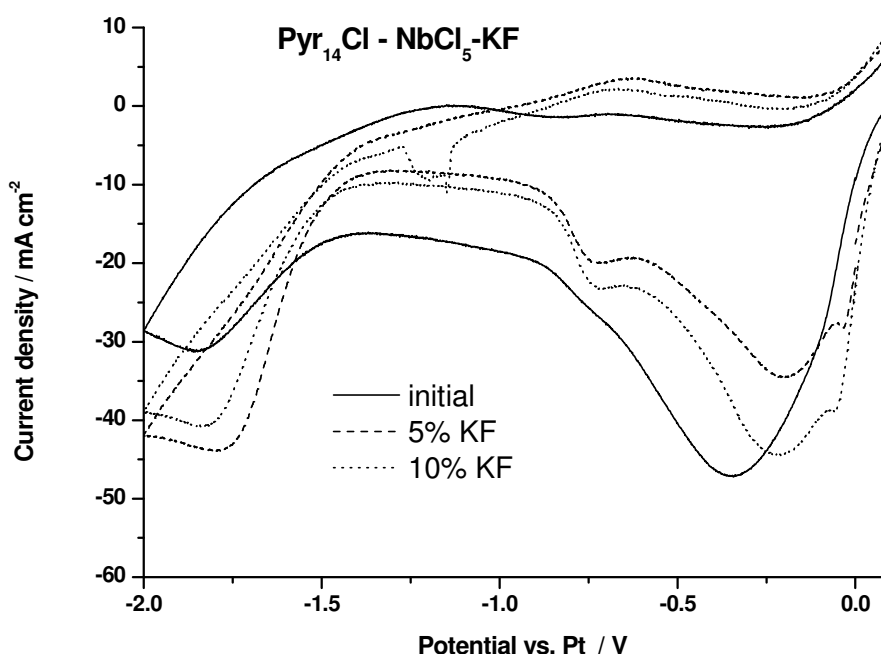


Figure 4.24. Cyclic voltammograms of $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ mixtures ($x=0.67$) with different amounts of KF additive: initial mixture (*solid curve*), 5 mole % KF (*dash curve*), and 10 mole % KF (*dot curve*)

Cyclic voltammograms of ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ($x=0.67$) with the additive of KF demonstrate the decrease of current density and the changes of the character of the reduction waves comparing to the initial mixture. In presence of 5-10 mole % KF one can observe two additional reduction peaks, at -0.10V and -1.75V. If we will compare the results obtained with above presented data, one can suggest the appearance of the additional amounts of Nb(IV) species in electrolyte.

4.1.3.2.2. Additives of CsF

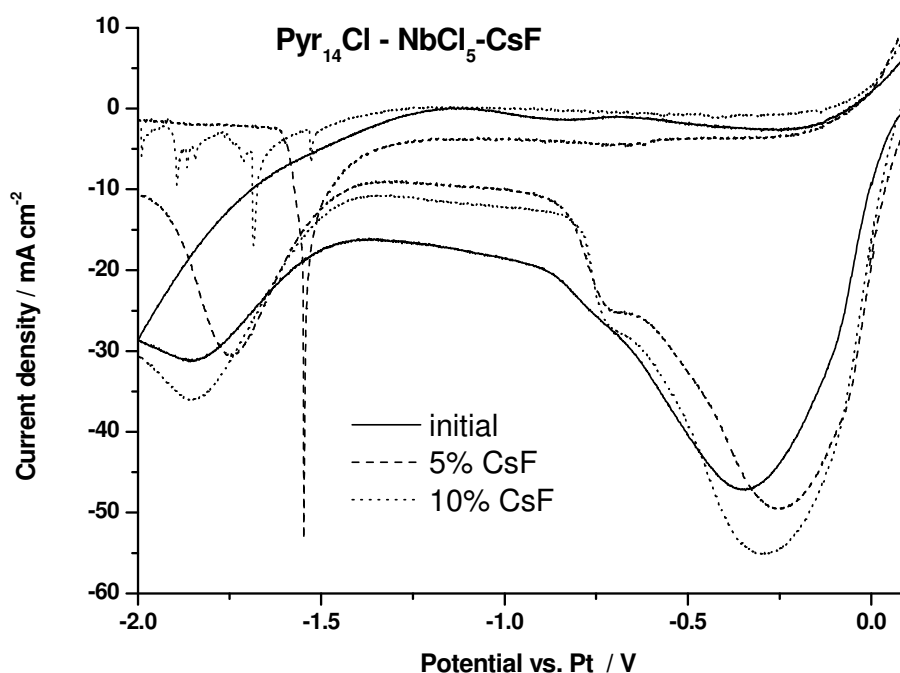


Figure 4.25. Cyclic voltammograms of (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures (x=0.67) with different amounts of CsF additive: initial mixture (*solid curve*), 5 mole % CsF (*dash curve*) and 10 mole % CsF (*dot curve*)

The presence of CsF does not change the character of cyclic voltammograms (*Figure 4.25. dash und dot curves*) demonstrating practically the same reduction mechanism of niobium (V) in ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ with or without additives of CsF. There are obviously three main reduction peaks in the cyclic voltammograms, the first at approx. -0.25V, the second at -0.75V and the third at -1.80V referred to Pt electrode. The first peak at -0.25 V is resolved more clear in two reduction waves when CsF was added. Some undesirable noises appear after the addition of CsF in the potential range from -1.50V to -2.00V. Therefore, one can conclude that the using of the additive of CsF does not lead to the significant improvement of electrolyte.

4.1.3.2.3. Additives of RbF

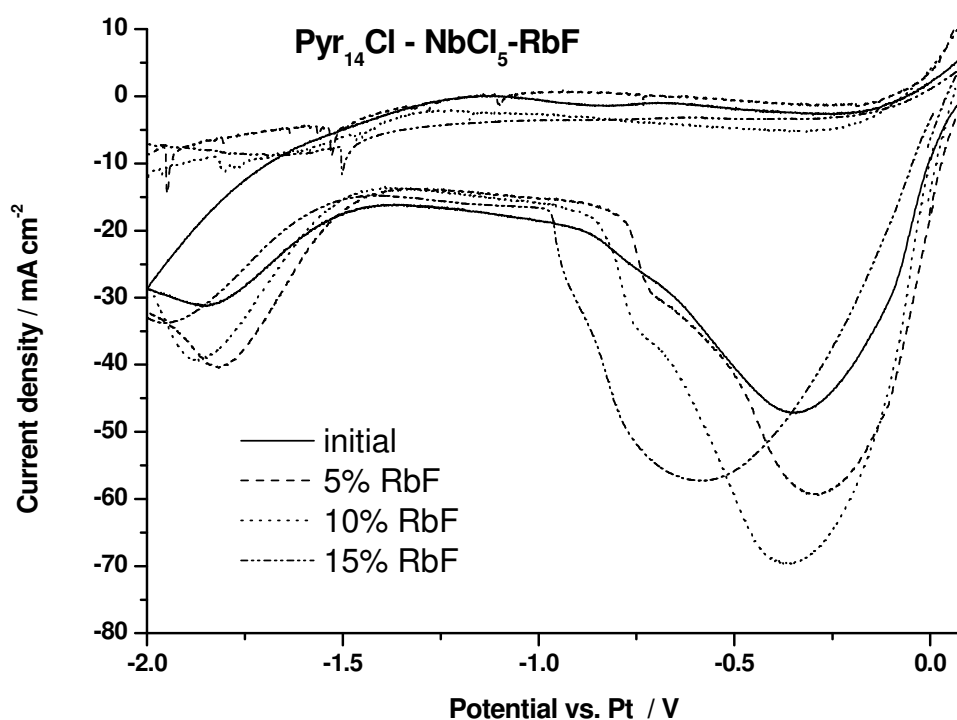


Figure 4.26. Cyclic voltammograms of (x)Pyr₁₄Cl-(1-x)NbCl₅ mixtures (x=0.67) with different amounts of RbF additive: initial mixture (*solid curve*), 5 mole % RbF (*dash curve*), 10 mole % RbF (*dot curve*) and 15 mole % RbF (*dash-dot-dot curve*)

The beneficial effect of the additive of RbF is observed: in the presence of 5 and 10 mole % RbF the electrical conductivity and, as a result the current density in the ionic liquid increases up to -70 mA/cm^2 . The further increase of the amount of RbF up to 15 mole % has an opposite effect: the current density decreases. Simultaneously the undesirable shift of the peak potentials towards cathodic direction is observed. Therefore, the ionic liquid Pyr₁₄Cl-NbCl₅-RbF at molar ratio of the components 60/30/10 was found the most promising candidate to electrochemical deposition of niobium.

4.1.3.3. Deposition experiments out of ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ with the additive of alkali metal fluoride

The ionic liquid $\text{Pyr}_{14}\text{Cl-NbCl}_5\text{-RbF}$ (60/30/10) was found to be the optimal composition for the deposition of niobium coatings. The experiments were carried out on the nickel plate substrate with the area of coverage 0.5024 cm^2 respectively. The specific form anode from pure niobium wire (diameter 1 mm, 99.8 % purity) purchased from Aldrich with the area of 0.2355 cm^2 was made additionally.

The constant current and pulse-interrupt deposition experiments were carried out in a two-electrode cell with temperature control at 140°C and the time of electrolysis was about 1h. The distance between cathode and anode was controlled about 3-5 mm according to the experimental cell geometry.

A series of the electrodeposition experiments were performed on the substrates made of platinum, gold, silver, and nickel. The most interesting result was obtained on nickel substrate using delay time t_{off} after deposition pulse at the constant potential. In this case a short pulse t_{on} (200 ms, $E_{\text{const}} = -2.3\text{V}$) was followed by the relatively long break time (400 ms) that allowed to refresh the ion concentration at the deposition interface between the pulses. The sample was characterized by ESEM/EDAX in the middle of the substrate and the results are presented in *Figure 4.27.-4.28*.

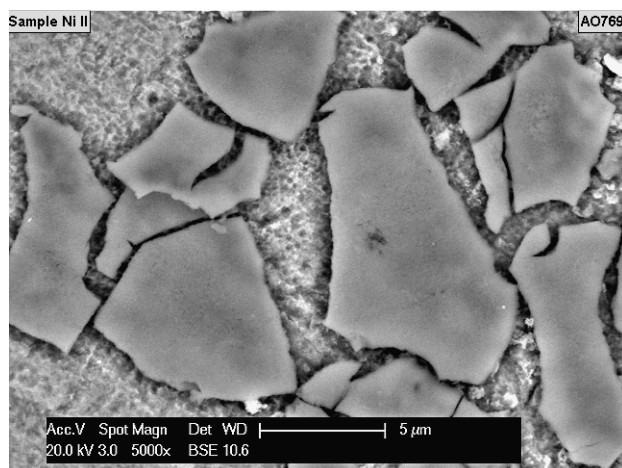


Figure 4.27. SEM micrograph of the deposit obtained during electroplating in the middle of the nickel substrate

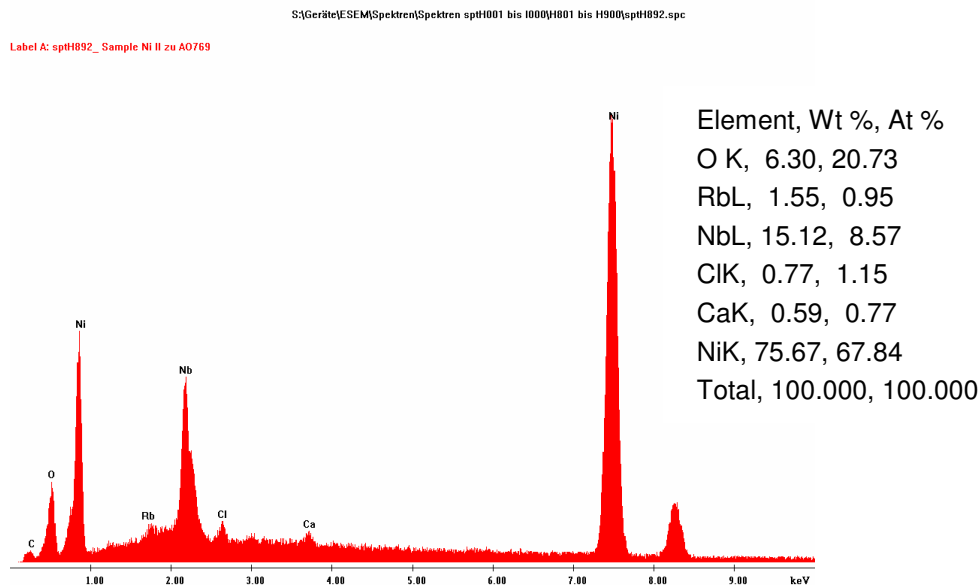


Figure 4.28. EDAX spectra of the surface in the middle of the nickel substrate

The plate-like deposits were obtained after 1 hour electrolysis out of ionic liquid $\text{Pyr}_{14}\text{Cl-NbCl}_5\text{-RbF}$ (60/30/10) on the nickel substrate. The deposit contains the plates of typically 8.57 atomic percent (at. %) of niobium and 20.73 at. % of oxygen (by EDAX analysis at *Figure 4.28.*) along with the 67.84 at. % of nickel, which is corresponding to the uncovered substrate (*Figure 4.27.*). Such high amount of oxygen presented in the deposit may originate from niobium oxides compounds most probably due to the additives of RbF. The formation of the latter is very difficult to avoid even working with high quality chemicals under inert atmosphere.

4.1.3.4. Conclusions

The influence of alkali metal halides, namely KF, RbF, and CsF on the reduction of niobium(V) in ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ ($x=0.67$) have been investigated in respect with the improvement of the electrochemical characteristic of electrolytes. On the base of cyclic voltamograms in the presence of 5-10 mole % of KF, 5-10 mole % of CsF, and 5-15 mole % of RbF it was found that the most promising composition for electrodeposition of niobium is the ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{NbCl}_5$ with 10 mole % RbF. The deposition experiments were carried out on platinum, gold, silver, and nickel substrates. The most interesting result was obtained on nickel substrate using the niobium soluble counter electrode.

Since no pure niobium was deposited, it can be concluded that in such ionic liquids metallic niobium is not formed during the electrolysis. A lot of work should be done to investigate the optimal parameters and to estimate the factors which are restricted the deposition processes. However, the main issue of this study was to elucidate the reduction mechanism which finally may lead to niobium metal deposition.

4.2. Ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$

4.2.1. Introduction

This chapter presents the results on spectroscopic and electrochemical investigation of ionic liquids based on 1-butyl-1-methylpyrrolidinium chloride with K_2NbF_7 salt in the range of composition $x=0.80\div 0.20$. These ionic liquids can be classified as “the mixed chloride-fluoride electrolytes”. “Fluoride electrolytes” (molten alkali metal fluorides with NbF_5 and K_2NbF_7 salts with common F^- anion) which are the most successful for high temperature electrodeposition of niobium coatings have no analogue in ionic liquids as the ionic liquids with simple F^- anion are not known till now. Ionic liquid with PF_6^- and BF_4^- anions can be considered as “fluoride electrolytes” in combination with NbF_5 and K_2NbF_7 salts. But for such types of ionic liquids one can expect the side chemical reactions between PF_6^- and BF_4^- anions and niobium(V) salts which complicate the electrochemical characterization.

The structure and composition of niobium(V) species in high temperature molten salts electrolytes is well investigated and this knowledge was used in the interpretation of the mechanism of electrochemical reduction. Concerning the using of ionic liquids as a media for electrochemical deposition of metallic niobium, there is still no reliable information about success in this area. There is also a lack of systematic spectroscopic investigation of niobium(V) species in ionic liquids used as electrolytes that gave us a strong motivation for present research.

4.2.2. Synthesis

1-Butyl-1-methylpyrrolidinium chloride (Pyr_{14}Cl) (Merck, high purity, content of moisture < 100 ppm, mp 203°C) is a white powder which starts to decompose after melting at ~ 210°C. It was dried for 48 hours under vacuum (0.003 mbar) at 80-95°C in flasks placed in an oil bath with stirring. The water content of Pyr_{14}Cl after drying was determined by Karl Fischer coulometric titration and was typically below 7-8 ppm. K_2NbF_7 (mp is not clear defined, but should be slightly above 700°C according to the literature, purity 99.5%) was purchased from Alfa Aesar and used as received.

Ionic liquids were prepared by combining Pyr_{14}Cl with a corresponding amount of K_2NbF_7 : they were mixed, placed in Pyrex tubes and melted in an electrical furnace in a glove box (Mbraun Star, O_2 and H_2O content below 3 ppm) under stirring. The process of formation of ionic liquids occurs in a very short temperature range. The mixtures $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ form milky-white opaque liquids at ~170-180°C in the basic-neutral range of compositions ($x=0.80\div0.50$). The acidic ionic liquids ($x=0.40\div0.20$) form the opaque gel-like mixtures at ~190°C. After melting, the samples were quenched in the inert atmosphere of the glove box.

4.2.3. Formation of ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇

Pyr₁₄Cl forms ionic liquids with different salts of niobium(V), NbCl₅ [190] and K₂NbF₇ in a wide range of concentration, namely at mole fractions of Pyr₁₄Cl equal to x=0.80-0.20. The ionic liquids exhibit an electrical conductivity in both basic and acidic ionic liquids and they can be classified as high concentrated non-aqueous electrolytes. Depending on the salt used, NbCl₅ or K₂NbF₇ the process of formation of ionic liquids differs significantly. In ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ with the common Cl⁻ anion the complex formation of various species was confirmed by means of *in situ* Raman spectroscopy [190]. *In situ* Raman spectroscopy at operating temperatures allows estimate the structure and composition of electrochemical active species. In basic mixtures at x=0.80, the self-reduction of Nb(V)→Nb(IV) was confirmed by Raman spectroscopy and [NbCl₆]²⁻ (75%) and [NbCl₆]⁻ (25%) octahedral complexes are the electrochemical active species at 140°C. At x=0.60, the dominant species are NbCl₆⁻ octahedra. In acidic ionic liquids at x=0.40, the electrochemical reduction of two species occurs, NbCl₆⁻ and Nb₂Cl₁₁⁻.

In the mixtures (x)Pyr₁₄Cl-(1-x)K₂NbF₇ the formation of ionic liquids is accompanied by more complicated process of the dissociation of K₂NbF₇ (Figure 4.29.) and leads to the formation of ionic liquids which possess the properties of electrolytes in basic and acidic range of concentration. To describe the structure and composition of the complex ions of niobium(V) introduced in the form of K₂NbF₇, one has to take into the consideration the data obtained in high temperature molten salts.

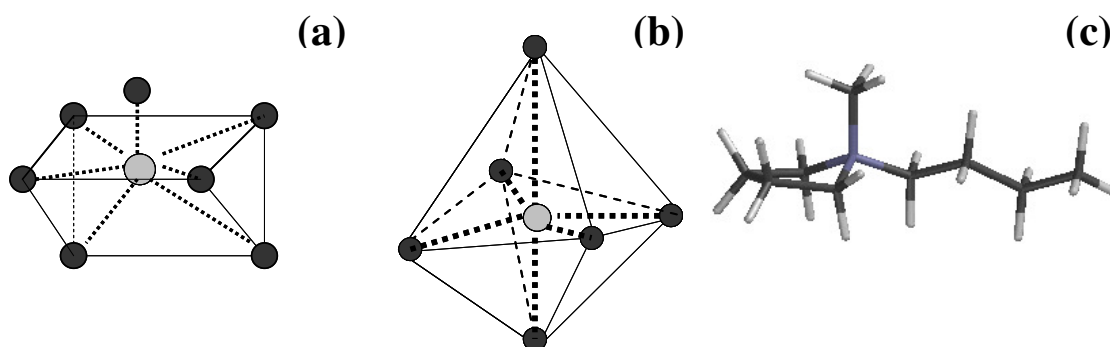


Figure 4.29. Structure of the complex ions [NbF₇]²⁻ (a), [NbF₆]⁻ (b), and pyrrolidinium ring cation, Pyr₁₄⁺ (c)

K_2NbF_7 consists of potassium ions and complex ions $[NbF_7]^{2-}$ of C_{2v} symmetry (*Figure 4.29. a*). The compounds K_2NbF_7 and K_2TaF_7 have the similar type structure. The lattice structure and the configuration of $[NbF_7]^{2-}$ and $[TaF_7]^{2-}$ was investigated by Hoard [166] and it was defined as a trigonal prism with six F^- ions at its vertices. The seventh F^- ion is situated above the centre of the rectangular place of the prism. Precise X-ray investigations, NMR, Raman, and IR studies were performed for above mentioned complexes in [191-193].

The structure and composition of niobium (V) fluoride and oxofluoride species was investigated in molten salts by means of Raman and IR spectroscopy. IR reflection spectra of Nb(V) in molten LiF-KF have demonstrated that $[NbF_7]^{2-}$ complex ion (555 cm^{-1}) is the predominant species [170]. The formation of $[NbF_7]^{2-}$ complex ion with C_{2v} structure in LiF-NaF-KF melt with vibrational frequencies $626, 371, \text{ and } 290\text{ cm}^{-1}$ was estimated by Raman spectroscopy [167, 168, 194, 195]. The existence of $[NbF_7]^{2-}$ complexes in the melts is the interesting contrast to the concentrated HF solutions (25-50 %HF) where only $[NbF_6]^-$ are the stable species [169]. The structure of $KNbF_6$ consists of potassium ions and $[NbF_6]^-$ complex ions which have the configuration of a distorted bi-pyramid (*Figure 4.29. b*) [196].

Despite the Raman data confirmed the presence only of $[NbF_7]^{2-}$ hepta-coordinated complex ions in fluoride melts, the dissociation of $[NbF_7]^{2-}$ according to the equation:



was investigated by Agulyansky [171 and references therein]. On the base of IR emission spectra of fluoride melts containing K_2TaF_7 and K_2NbF_7 , it was demonstrated that their most common property is the equilibrium between hexa- and hepta-coordinated complexes, $[MeF_6]^-$ and $[MeF_6X]^{(n+1)-}$ ($Me = Ta, Nb; X^{n+} = F^-, Cl^-, Br^-, I^-, O^{2-}$). In general, the equilibrium is defined by concentration of the components, by the nature of X ions, and outer-sphere cations.

In basic ionic liquids $(x)Pyr_{14}Cl-(1-x)K_2NbF_7$ ($x>0.50$), $Pyr_{14}Cl$ (*Figure 4.29. c*) is the solvent for K_2NbF_7 . In acidic ionic ($x<0.50$), the molecule of $Pyr_{14}Cl$ are introduced in the crystal lattice of K_2NbF_7 .

The following schemes of complex formation – dissociation might be considered:



Even in the excess of Cl^- anions, the formation of mixed fluoride-chloride complexes seems unlikely. In basic ionic liquids, at $x \leq 0.80$ the shift of the reaction (4.15) towards the formation of octahedral complexes NbF_6^- is the most probable according to the Ostwald's dilution law. As a slightly gas evolution had accompanied the formation of ionic liquid at $x=0.80$, it can be the indirect confirmation of the reactions (4.15) and (4.16). As the concentration of K_2NbF_7 increases, the dissociation has to be suppressed.

4.2.4. FTIR and Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$: composition dependence

FTIR spectra of solid ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ in the range of $x=0.80-0.20$ are presented in Figure 4.30. As Pyr_{14}Cl does not exhibit any vibrations in the range $400-700\text{ cm}^{-1}$, new bands observed at $535-545\text{ cm}^{-1}$ and $608-612\text{ cm}^{-1}$ are due to the different niobium (V) complexes. The band at $\sim 540\text{ cm}^{-1}$ is assigned to $[\text{NbF}_7]^{2-}$ hepta-coordinated complex anion and at $\sim 610\text{ cm}^{-1}$ - to $[\text{NbF}_6]^-$ octa-coordinated one. FTIR spectra of ionic liquids in concentration range $x=0.80-0.20$ demonstrate the gradual change of the equilibrium between $[\text{NbF}_7]^{2-}$ and $[\text{NbF}_6]^-$ complexes: it shifts towards $[\text{NbF}_7]^{2-}$ complex ions as the molar fraction of K_2NbF_7 increases.

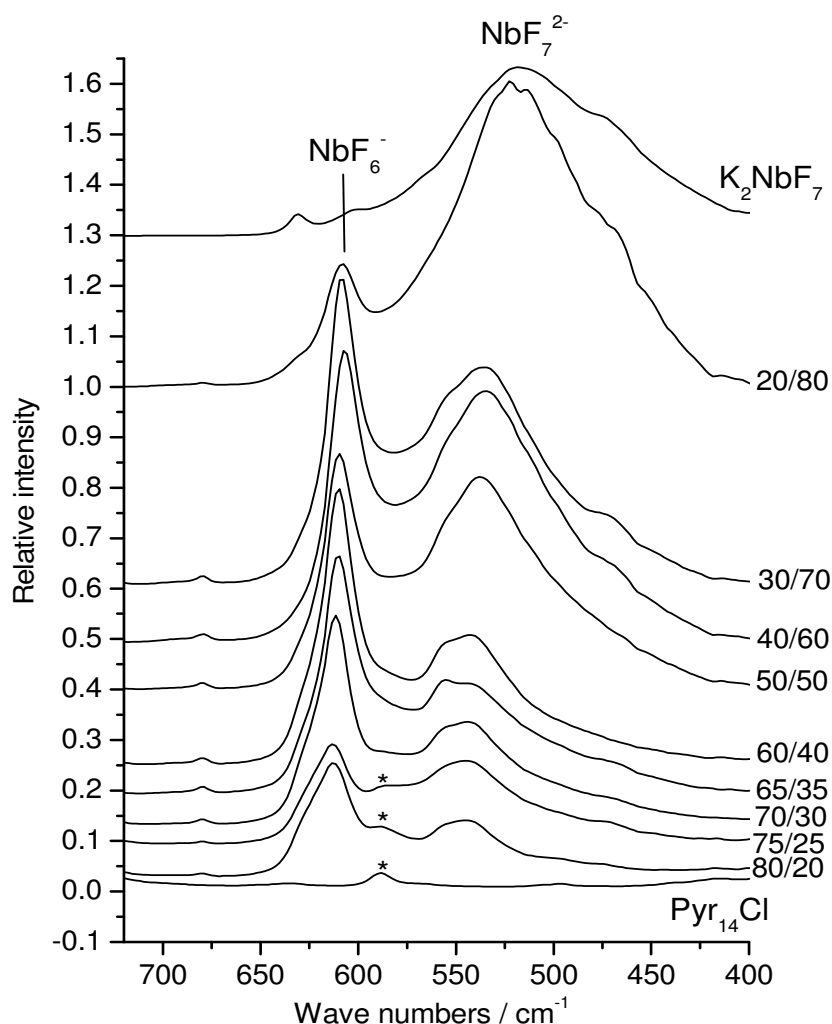


Figure 4.30. FTIR spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ ($x=0.80-0.20$) in the solid state at 20°C : concentration dependence (the band of Pyr_{14}Cl is marked with asterisk*)

Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ in the range of $x=0.80-0.20$ are presented in *Figure 4.31*. Pyr_{14}Cl has no vibrations in the range $400-700\text{ cm}^{-1}$ and the new bands observed in this range are attributed to different niobium (V) complexes. Raman spectra confirm the presence of two niobium species, $[\text{NbF}_7]^{2-}$ ($\sim 630\text{ cm}^{-1}$) and $[\text{NbF}_6]^-$ ($\sim 680\text{ cm}^{-1}$) over the full concentration range but the correlation between two of them differs from the peculiarity obtained on the base of FTIR spectra.

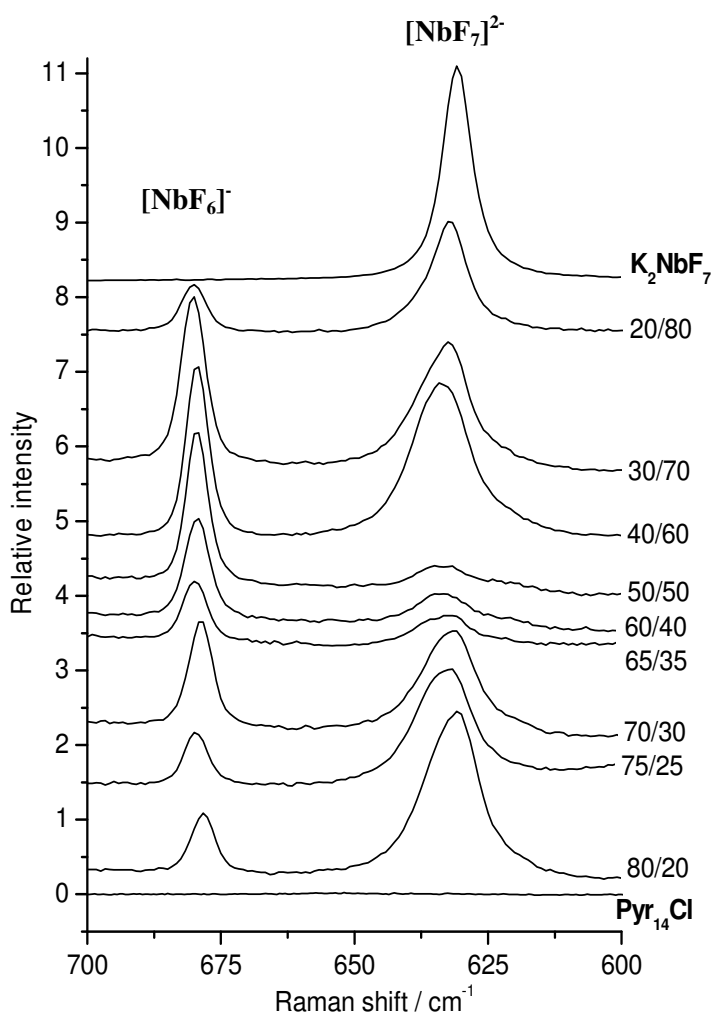


Figure 4.31. Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ ($x=0.80-0.20$) in the solid state at 20°C : composition dependence

The FTIR and Raman spectra were evaluated by computer-resolving the bands into sums of Gaussians functions in the range $700-300\text{ cm}^{-1}$ to estimate the distribution of $[\text{NbF}_7]^{2-}$ and $[\text{NbF}_6]^-$ species in ionic liquids. The calculations for FTIR and Raman spectra were done

on the base of the assignment of vibrations of niobium(V) species as it was described above. The content of $[\text{NbF}_6]^-$ species in ionic liquids depending on the molar composition are presented in *Figure 4.32*.

The data obtained by means of FTIR and Raman spectroscopy are not fully in agreement. According to the FTIR spectra, the content of $[\text{NbF}_6]^-$ species reduces gradually from 62 % ($x=0.80$) up to 15 % ($x=0.20$) as the concentration of K_2NbF_7 increases (*Figure 4.32. a*).

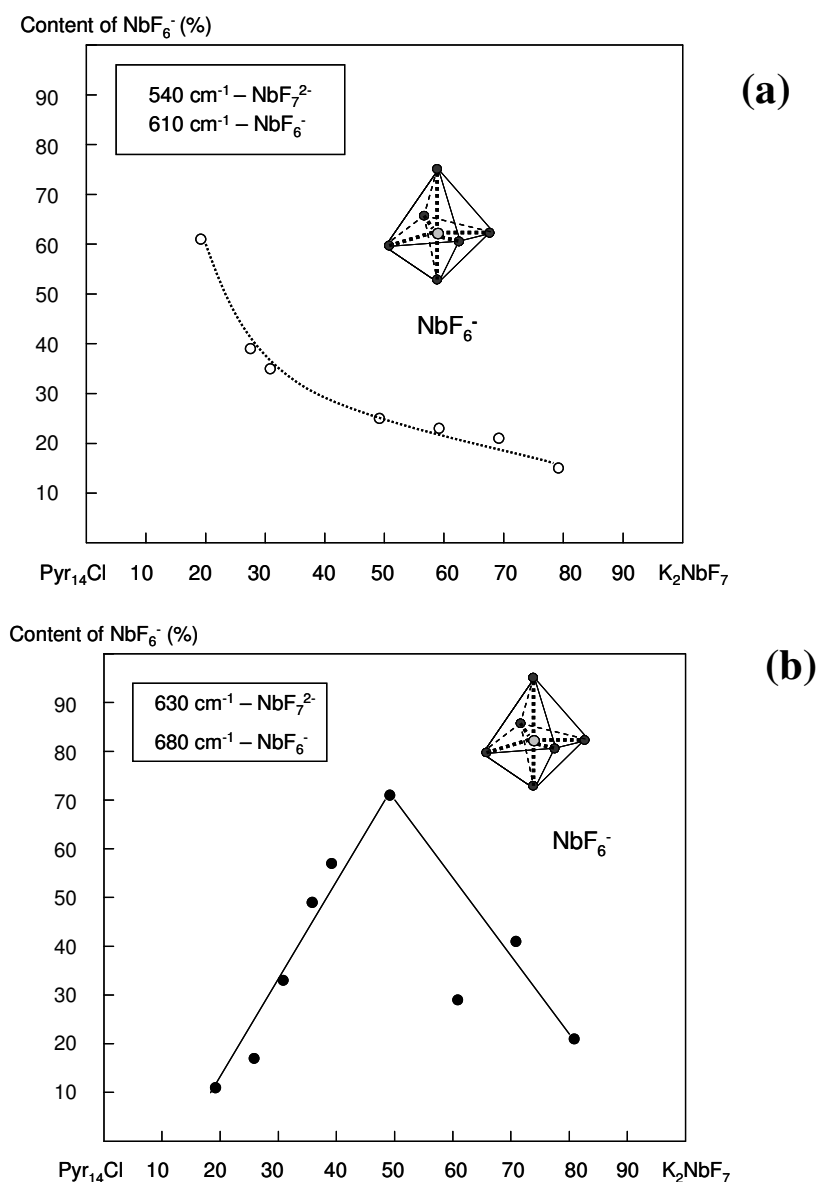


Figure 4.32. Content of $[\text{NbF}_6]^-$ species in ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ ($x=0.80-0.20$) evaluated by computer resolving the peaks into the sums of Gaussian functions on the base of FTIR **(a)** and Raman spectra **(b)**

In contrast to FTIR data, the Raman spectra of basic ionic liquids ($x=0.80-0.70$) demonstrate the domination of $[\text{NbF}_7]^{2-}$ species (*Figure 4.32. b*). The equilibrium between $[\text{NbF}_7]^{2-}$ and $[\text{NbF}_6]^-$ is shifted towards $[\text{NbF}_6]^-$ species. Their content increases from 13% up to 70% passing from $x=0.80$ to $x=0.50$ and reaches its maximum content at $x=0.50$. In acidic ionic liquids, passing from $x=0.50$ to $x=0.20$ the content of $[\text{NbF}_6]^-$ complexes reduces up to 20 % at $x=0.20$.

Such contra-dictionary may originate from the changes of the structure of ionic liquids with K_2NbF_7 salt occurring slowly in a solid state. One has to mention the specific feature of basic $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ ionic liquid in access of Pyr_{14}Cl at $x=0.80$, namely that the spectral characteristics of the same sample are changed depending on the time of the storage. The Raman spectrum of the sample at $x=0.80$ obtained directly after synthesis may differ from the Raman spectrum recorded in a few days. In detail it means: Raman spectrum was recorded in a sealed Duran tube after synthesis under inert atmosphere, the tube was stored in a glove box and the Raman spectrum was taken again in a few days. The spectra were recorded from different points to confirm the homogeneous of ionic liquids and the reproducibility of the spectra. The Raman spectra of ionic liquid at $x=0.80$ recorded directly after synthesis and in 2 days are presented in *Figure 4.33*.

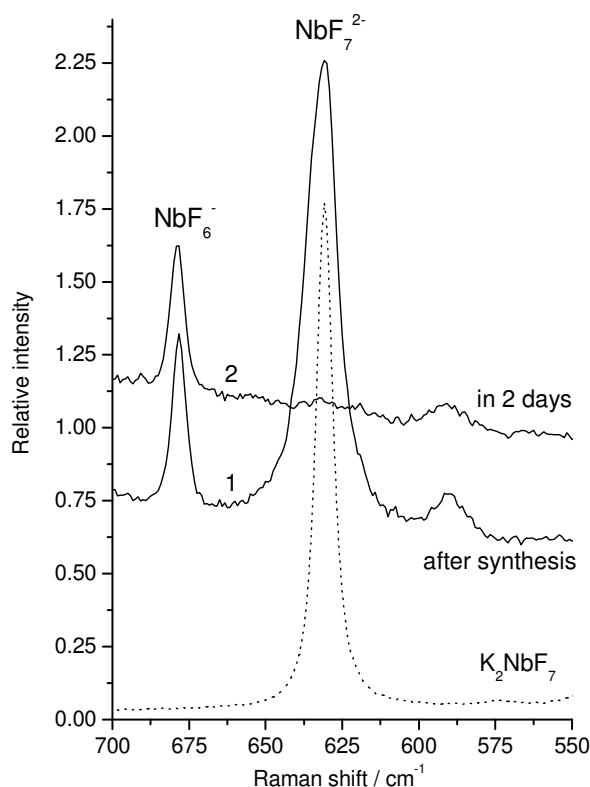


Figure 4.33. Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.80$: 1- after synthesis; 2 – in 2 days

The Raman spectrum of the sample in 2 days demonstrates the disappearance of the vibration at 631 cm^{-1} assigned to $[\text{NbF}_7]^{2-}$ complex ion. As the intensity of the vibration of $[\text{NbF}_6]^-$ (678 cm^{-1}) species remains constant, the observed changes cannot be connected with the equilibrium between $[\text{NbF}_6]^-$ and $[\text{NbF}_7]^{2-}$ species. The ratio of $\text{NbF}_6^- / \text{NbF}_7^{2-}$ after synthesis was calculated to be 14/86 (%) and after 2 days it was changed to $\sim 100 / 0$ (*Table 4.6.*).

The plausible explanation of this phenomenon may consist in the loss of the identity of the hepta-coordinated complex ions NbF_7^{2-} surrounded by large organic pyrrolidinium ring cations, most probably due to the formation of different ionic pairs and more complicated aggregates which are not detectable by spectroscopic methods. This phenomenon was observed only for basic ionic liquids at $x \approx 0.80$.

4.2.5. *In situ* Raman spectra of basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇: temperature dependence

Investigation of the temperature dependence of Raman spectra of ionic liquids provide the valuable information about the structure and composition of electrochemical active species of niobium(V) at operating temperatures and can give insight in the mechanism of electrochemical reduction of niobium(V). *In situ* Raman spectra of ionic liquids (x)Pyr₁₄Cl-(1-x) K₂NbF₇ at x=0.80; 0.65; 0.60; 0.40 were recorded in temperature range 20-200°C and the general view is presented in Figure 4.34.

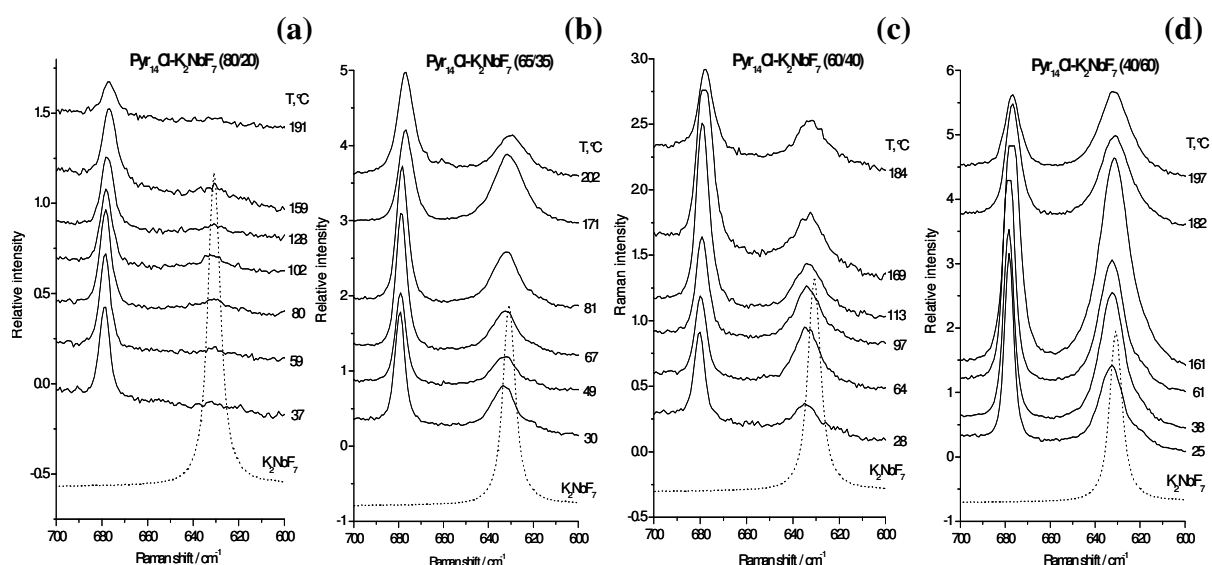


Figure 4.34. The general view of *in situ* Raman spectra of ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇: temperature dependence (20-200°C): (a) – x=0.80; (b) – x=0.65; (c) – x=0.60; (d) – x=0.40

More detailed views of *in situ* Raman spectra for each composition are presented in Figures 4.35. – 4.38.

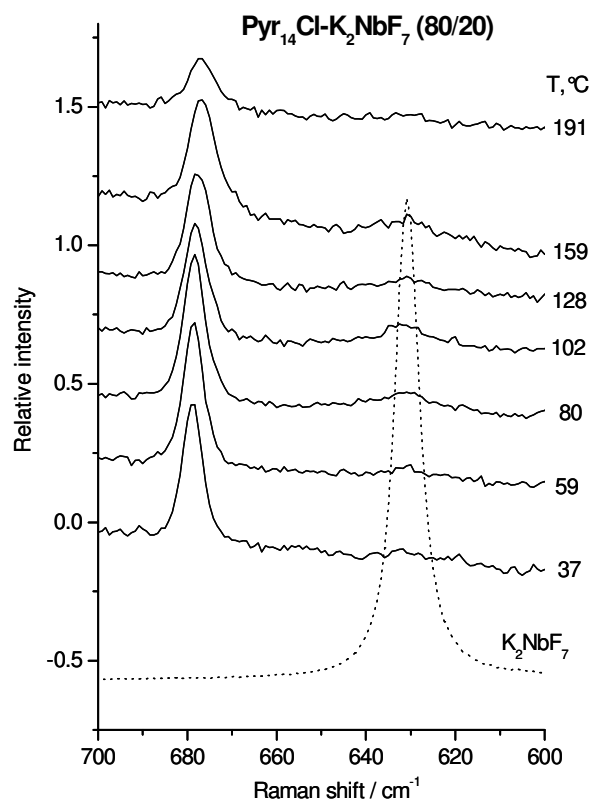


Figure 4.35. *In situ* Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.80$: temperature dependence (20-200°C)

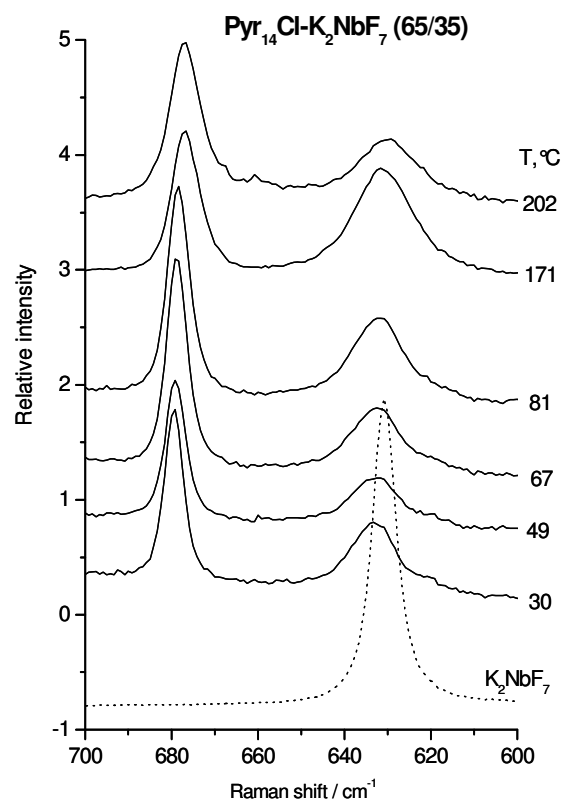


Figure 4.36. *In situ* Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.65$: temperature dependence (20-200°C)

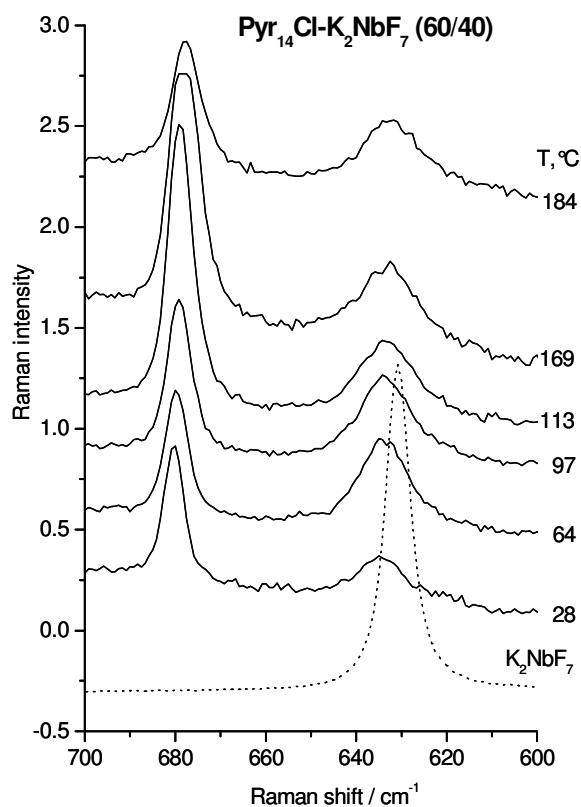


Figure 4.37. *In situ* Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.60$: temperature dependence (20-200 $^{\circ}\text{C}$)

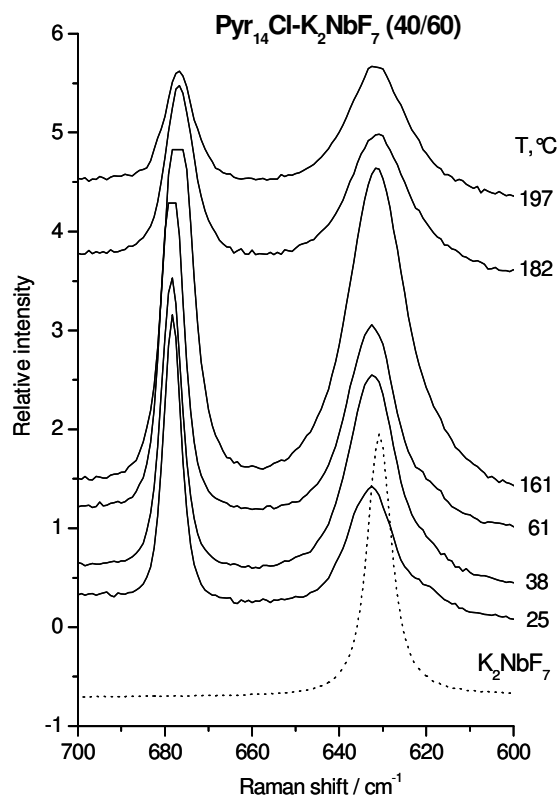


Figure 4.38. *In situ* Raman spectra of ionic liquids $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.40$: temperature dependence (20-200 $^{\circ}\text{C}$)

In basic ionic liquids at $x=0.80$ (*Figure 4.35.*) the dominant niobium(V) species are NbF_6^- complex ions. Very weak band at 630 cm^{-1} assigned to NbF_7^{2-} ions appears at 159°C and it corresponds to the increase of the content of NbF_7^{2-} ions from about 0 at room temperature up to 28 % as the temperature rises.

Ionic liquids at $x=0.65$, 0.60, and 0.40 (*Figures 4.36. – 4.38.*) exhibit the vibration of both, NbF_6^- and NbF_7^{2-} ions in a solid state at room temperature and in molten state. The correlation between these two complex ions was estimated on the base of Gaussian curves and the data are collected in *Table 4.6.*

Table 4.6. Content of NbF_6^- and NbF_7^{2-} complex ions in ionic liquids at different compositions at room temperature and at operating temperatures $160\text{--}170^\circ\text{C}$ (estimated on the base of Gaussian distribution curves)

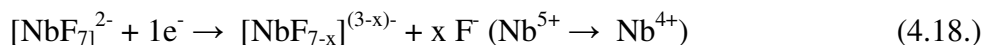
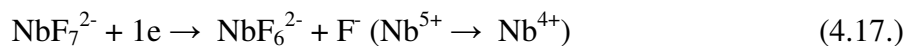
Composition	80/20	65/35	60/40	40/60
Content of complex ions, %	$\text{NbF}_6^- / \text{NbF}_7^{2-}$	$\text{NbF}_6^- / \text{NbF}_7^{2-}$	$\text{NbF}_6^- / \text{NbF}_7^{2-}$	$\text{NbF}_6^- / \text{NbF}_7^{2-}$
30°C	$\sim 100 / 0$	$53 / 47$	$64 / 36$	$45 / 55$
$160\text{--}170^\circ\text{C}$	$72 / 28$	$40 / 60$	$65 / 35$	$36 / 64$

4.2.6. Electrochemical measurements of ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇

On the basis of *in situ* Raman spectroscopic data, the co-existence of two species of niobium(V), NbF₆⁻ and NbF₇²⁻ was confirmed in both basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at operating temperatures 160-170°C. Therefore the investigation of the mechanism of electrochemical reduction was concentrated at the composition at x=0.65.

Information on the electrochemical reduction of niobium(V) in high temperature molten salt electrolytes can be helpful in the interpretation of the electrochemical behaviour of niobium(V) in ionic liquids. Electrochemical reduction of niobium(V) in fluoride electrolytes was investigated in [123-129, 138]. The influence of oxide on the chemical and electrochemical behaviour of niobium ions in molten fluorides was studied by a number of researchers [127-129]. The formation of niobium(V) hepta-coordinated complexes, NbF₇²⁻ in high temperature diluted fluoride electrolytes was confirmed by spectroscopy [167, 168, 170, 171, 194, 195] and these species were taken into consideration in the clarification of the mechanism of electrochemical reduction of niobium(V). Their reduction from alkali fluoride electrolyte is discussed via a three steps reduction mechanism [123, 124] whereby the first is a reversible one-electron transfer Nb⁵⁺ → Nb⁴⁺ at -0.11 V (referred to the Ni/Ni²⁺ electrode) followed by a reversible three-electron step to the monovalent state at -0.76 V. The third final step is an irreversible one-electron reduction to the metal state at -1.02 V. To obtain coherent metal deposition, the mean valence must be reduced to approximately four in the initial electrolyte.

The data of authors [123, 124, 126-128] are in agreement concerning the first reduction step, namely Nb(V) to Nb(IV) for NbF₇²⁻ species. This step was considered to lead to the formation of octahedral species NbF₆²⁻ or [NbF_{7-x}]^{(3-x)-} species, accompanying by the formation of free F⁻ anion according to the equation (4.17.) [128] or to the equation (4.18.) [124]:



The further reduction steps occur with the participation of [NbF_{7-x}]^{(3-x)-} or NbF₆²⁻ species and with possible formation of the intermediate compound NbF (liquid or solid). Finally, irreversible reduction to metallic niobium occurs at the potentials more negative than

-1.0 V referred to the Ni/Ni^{2+} electrode [123, 124, 128]. Contrary to the three step mechanism of niobium(V) reduction, a two-step reduction process $\text{Nb(V)} \rightarrow \text{Nb(IV)} \rightarrow \text{Nb(0)}$ was suggested in [126].

Mixed chloride-fluoride electrolytes have been studied under two conditional categories: solutions of K_2NbF_7 in molten eutectic NaCl-KCl or NaCl-KCl-KF melts [137, 139, 142, 143] and molten fluoride bath LiF-NaF with NbCl_5 as a source of niobium ions [138, 141].

The mechanism of electrodeposition of niobium from K_2NbF_7 solution in molten NaCl-KCl at 720°C was studied in [143]. It was shown that the reaction proceeds in two steps: first a reversible redox reaction, $\text{Nb(V)} + e \leftrightarrow \text{Nb(IV)}$ followed by a quasi-reversible reduction, $\text{Nb(IV)} + 4e \rightarrow \text{Nb(0)}$ at the potentials 0.394V and -0.178V vs. the Ni/Ni^{2+} reference electrode, respectively. The similar two sequential stages: $\text{Nb(V)} \xrightarrow{\text{rev}} \text{Nb(IV)} \xrightarrow{\text{quasi-rev}} \text{Nb(0)}$ have been proposed by Polyakova and Taxil [142] as the explanation of the process mechanism in the NaCl-KCl-KF melt with K_2NbF_7 addition at 700°C .

In reference [137] it had been shown that the solution of K_2NbF_7 in molten NaCl-KCl was not stable and underwent a slow chemical reduction to Nb(IV) . Therefore, Nb(IV) as the stable species found in the melt was reduced to Nb via a slow four-electron exchange step at around -0.5V vs. AgCl/Ag .

The system LiF-NaF-NbCl_5 was used for electrolytic deposition of niobium [138, 141] and the following reduction mechanism was proposed: $\text{Nb(V)} \leftrightarrow \text{Nb(IV)} \rightarrow \text{Nb(0)}$ which is in a good agreement with the previous authors.

4.2.7. Cyclic voltammetry of basic ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65: temperature dependence

The solidified ionic liquid under repeated heating is getting liquid below 100°C. Under this temperature condition, it exhibits very low electrical conductivity because of the high viscosity and low mobility of ionic species. Cyclic voltammograms of ionic liquid were recorded starting from 100°C up to 180°C at 10°C interval and the selected cyclic voltammograms are presented in *Figure 4.39*. They demonstrate the gradual increase of current density as the temperature rises. The optimal operating temperature where one can obtain the resolution of redox peaks at the maximum of current densities was found to be 160-170°C. The further increase of the temperature does not influence the character of cyclic voltammograms and current density but can lead to the decomposition of ionic liquid.

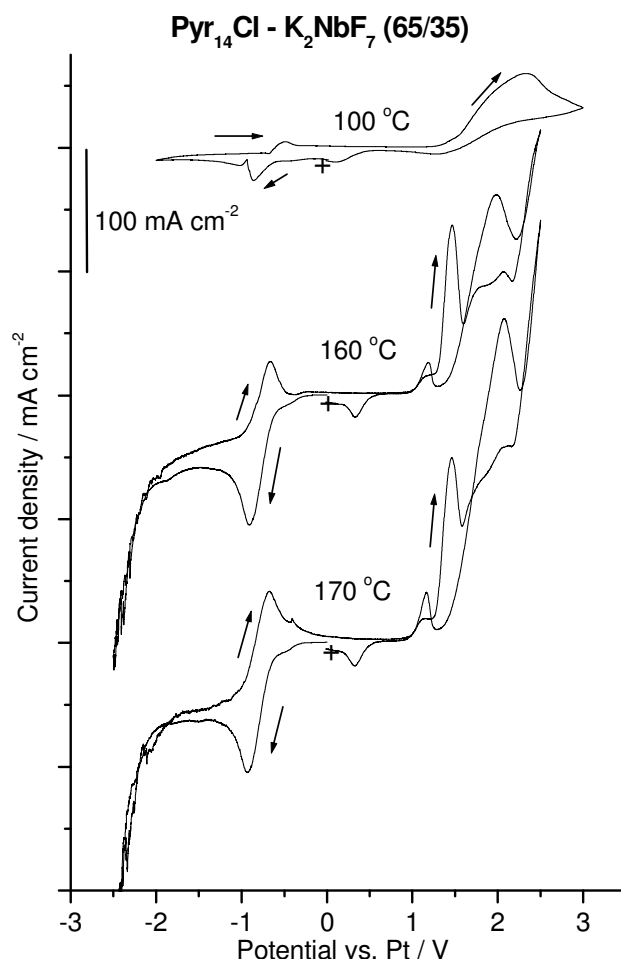


Figure 4.39. Temperature dependence of cyclic voltammograms of ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65 (T=110-170°C; WE-Pt disc; CE-GC; RE-Pt wire; scan rate 100 mV s⁻¹)

4.2.8. Cyclic voltammetry of basic ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65 : various potential ranges

Cyclic voltammograms of basic ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65 were recorded at 170°C with various expansion in the potential range from -3.0 V to 3.0 V started from OCP (about 0 V vs. Pt) in the cathodic direction (*Figure 4.40.*). The first redox couple R₁/O₁ appears in the negative potential range: R₁ at -0.90 V and O₁ at -0.66 V and its position remains constant within enlargement of the potential window. The second redox couple is observed at more negative potentials: R₂ at -1.74 V and O₂ at -1.55 V. The redox couple R₃/O₃ appears in the positive potential range, namely R₃ at 0.31 V and O₃ at 1.43 V and also remains unchanged between various potential windows.

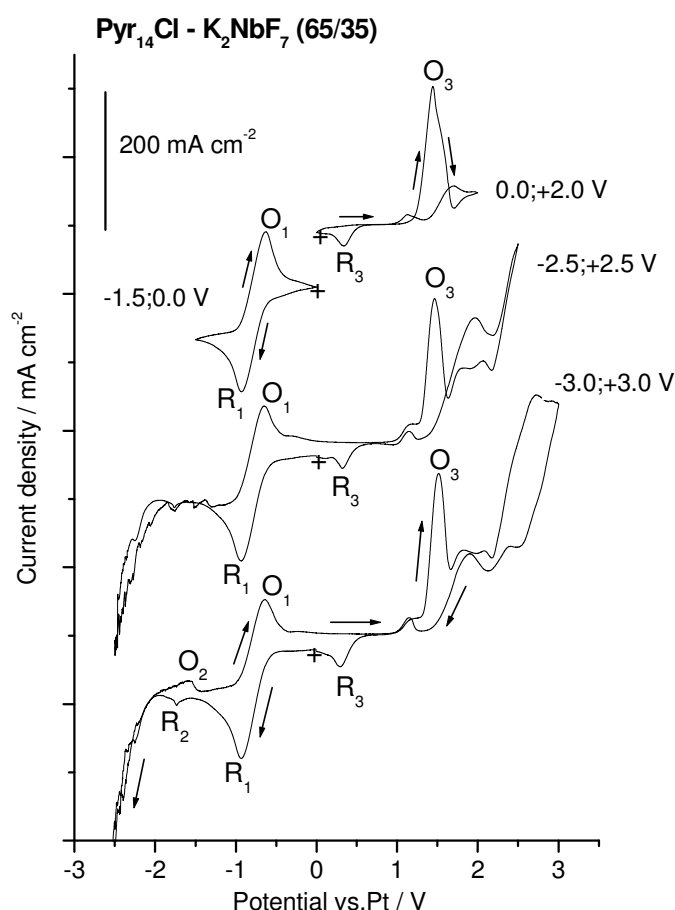


Figure 4.40. Cyclic voltammograms of ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65 recorded between different potential windows (T=170°C; scan rate 200 mV s⁻¹; WE-Pt disc; CE-GC; RE-Pt wire)

4.2.9. Cyclic voltammetry of basic ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65 : analysis of redox couples

In order to get insight into the reversibility of the redox process R₁/O₁, it has been studied within narrow bounds from -1.5 V to 0.0 V at different scan rates at 170°C (Figure 4.41.). In first approximation the peak currents of the reduction and oxidation peaks are apparently proportional to the square root of the scan rate consistent with diffusion control (Figure 4.42. a). Both the cathodic and anodic peak potentials are only slightly dependent on the scan rate: the peak potential of the cathodic wave, R₁ slightly shifts to more negative values and the oxidation wave, O₁ slightly moves to the positive direction with increase of the scan rate (Figure 4.42. b and Table 4.7.).

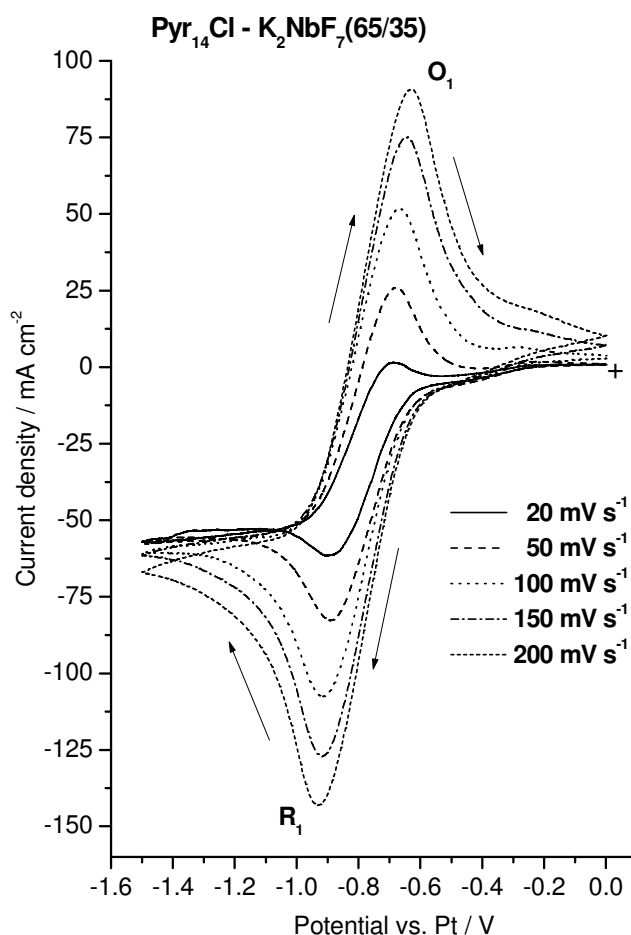


Figure 4.41. Cyclic voltammograms of the (x)Pyr₁₄Cl-(1-x)K₂NbF₇ ionic liquid at x=0.65 recorded at different scan rate for the first redox couple R₁/O₁ (T=170°C, scan rate 20÷200 mV s⁻¹; WE-Pt disc; CE-GC; RE-Pt wire)

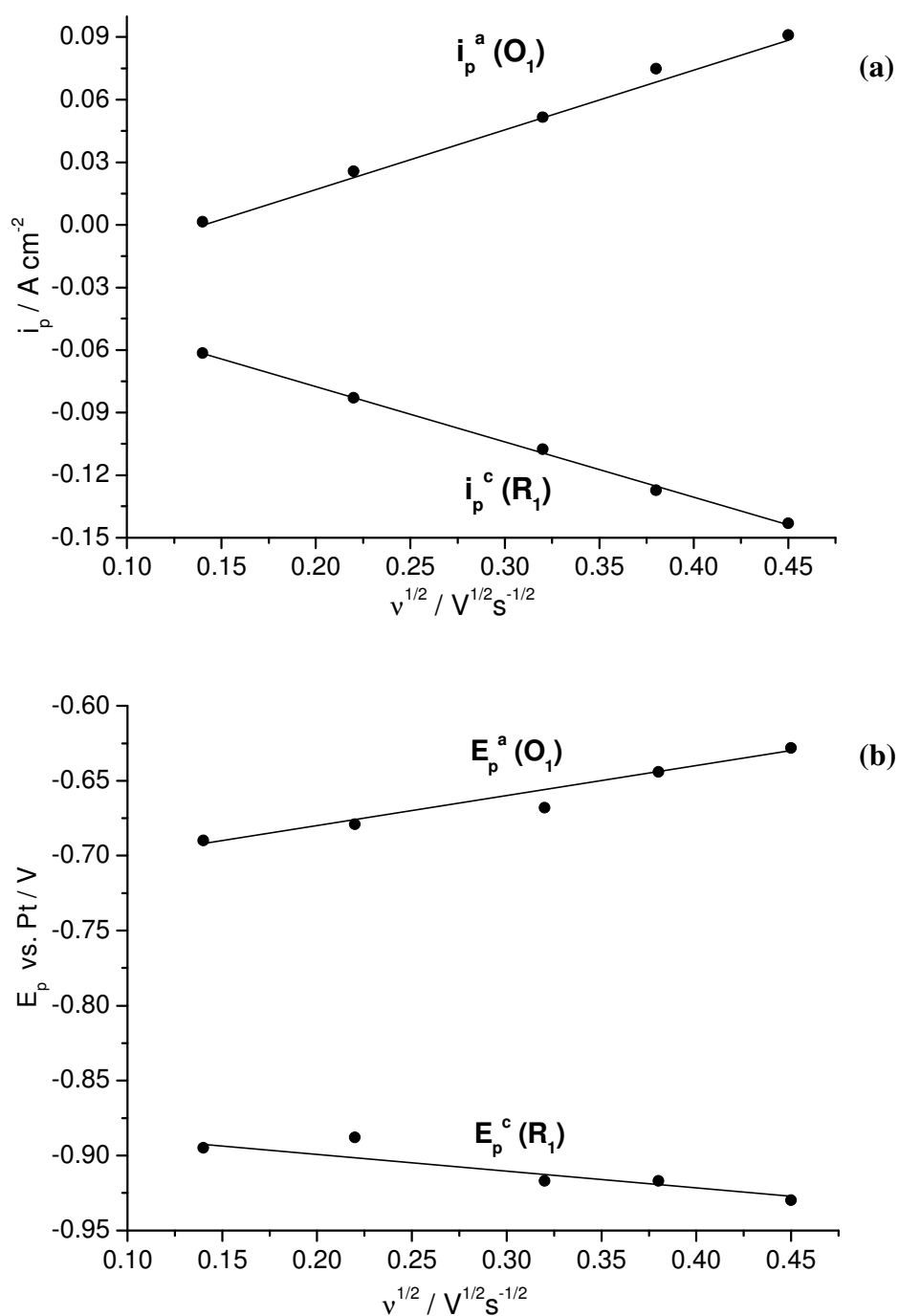


Figure 4.42. Correlation between the current densities (i_p) of the waves R_1 and O_1 and the square root of the scan rate ($v^{1/2}$) (a); correlation of peak potentials (E_p) of the waves R_1 and O_1 and the square root of the scan rate ($v^{1/2}$) (b)

Table 4.7. Cyclic voltammetric data for the redox process R_1/O_1 of niobium(V) in the $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ mixture at $x=0.65$ (potential window $-1.5 \div 0.0\text{V}$) for different scan rates ν . Potential vs. Pt

$\nu/$ [V s ⁻¹]	$\nu^{1/2}/$ [V ^{1/2} s ^{-1/2}]	$i_p^c(R)/$ [A cm ⁻²]	$i_p^a(O)/$ [A cm ⁻²]	PR	E_p^c / [V]	E_p^a / [V]	E^0 / [V]
0.02	0.14	-6.153×10^{-2}	0.134×10^{-2}	0.021	-0.895	-0.690	-0.792
0.05	0.22	-8.296×10^{-2}	2.568×10^{-2}	0.309	-0.888	-0.680	-0.784
0.10	0.32	-10.764×10^{-2}	5.158×10^{-2}	0.479	-0.917	-0.668	-0.792
0.15	0.38	-12.733×10^{-2}	7.483×10^{-2}	0.587	-0.917	-0.644	-0.780
0.20	0.45	-14.314×10^{-2}	9.086×10^{-2}	0.634	-0.930	-0.628	-0.779

Where, $E^0 = (E_p^a + E_p^c) / 2$ is called formal potential for a couple.

Peak current ratio $\text{PR} = |i_p^a / i_p^c|$

The peak current ratio is not equal or close to 1 as it could be expected for a simple reversible couple. This declares that the peak ratio can be affected by chemical reactions accompanying the redox process. Also the peak separation is sufficiently large ($\Delta E^0 > 150$ mV) which indicates that the electrode process is more complicated than the appearance of the cyclic voltammogram. In conclusion, these observations indicate that the redox process R_1/O_1 is not a simple reversible one. Possibly, two electrochemical active species of niobium(V), NbF_7^{2-} and NbF_6^- participate in the electrochemical reduction at close potentials. The NbF_7^{2-} complexes are present in the electrolyte at 170°C with an amount of $\sim 60\%$. As the hepta-coordinated complexes of niobium(V), NbF_7^{2-} possess a lower symmetry and, presumably, a lower strenght of the Nb-F bond than the octahedral species, NbF_6^- they are expected to be reduced at more positive potentials in comparison with the latter one. With this assumption it is reasonable to assign the redox couple R_1/O_1 to the reduction reaction of both species, NbF_7^{2-} and NbF_6^- .

The origin of the weak redox couple R_2/O_2 is not clear yet. In analogy with high temperature studies, it may be due to NbF formation (see above); however, this must be confirmed by further investigations. The strong decrease of cathodic currents below -2.0 V (*Figure 4.40.*) is indicative for niobium metal deposition; it exhibits the main features of Nb(0) deposition in high temperature molten salts, *e.g.* the potential distance from the

Nb(V)/Nb(IV) redox potential. In how far it is overlapped by potassium metal deposition is unclear.

Concerning the redox couple R_3/O_3 , a strong oxidation peak at 1.43 V is attributed to irreversible oxidation of Cl^- anions with chlorine gas evolution. An insignificant corresponding reduction peak at 0.31 V can be assigned in this case to the negligible reduction of Cl_2 which remains in ionic liquids into Cl^- anions [190, 149].

Cyclic voltammograms of ionic liquid $(x)Pyr_{14}Cl-(1-x)K_2NbF_7$ at $x=0.65$ recorded between different potential windows, $-1.5\text{ V} \div 0\text{ V}$ and $-3.0\text{ V} \div 3.0\text{ V}$ are presented in *Figure 4.43*. They demonstrate the good correspondence of the redox couple R_1/O_1 recorded under different conditions. One can also observe that the area of the reduction peak, R_1 is reduced and the area of the oxidation peak, O_1 is increased between narrow potential windows ($-1.5\text{ V} \div 0\text{ V}$). Also under such conditions the electrochemical process is getting more reversible.

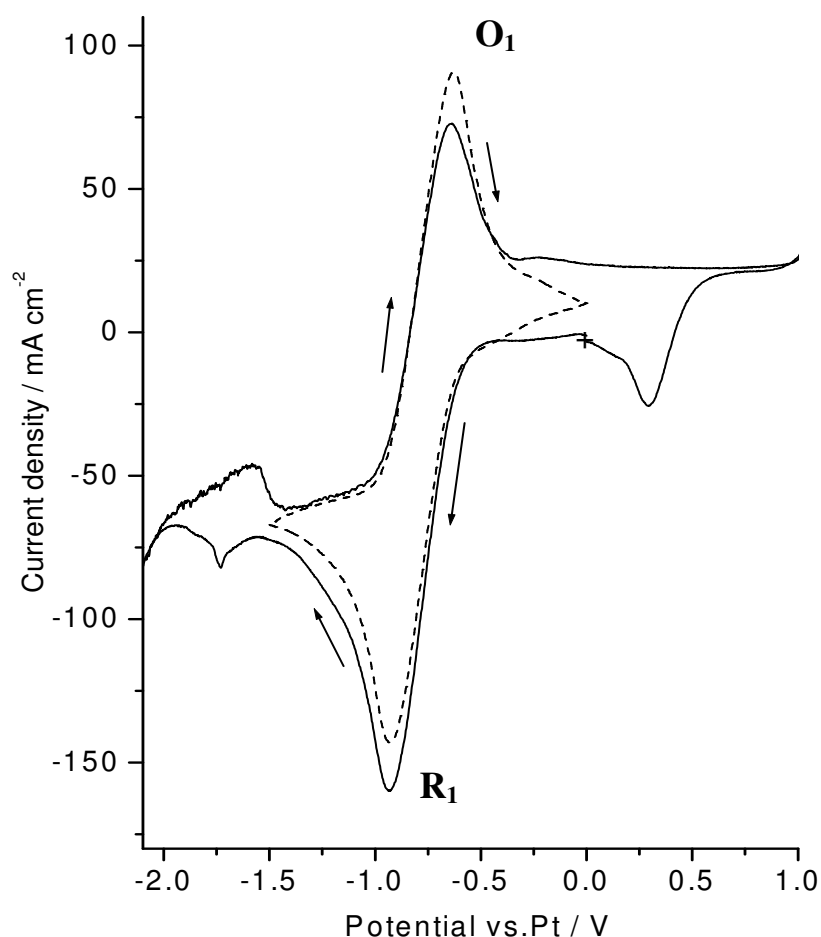


Figure 4.43. Cyclic voltammograms of ionic liquid $(x)Pyr_{14}Cl-(1-x)K_2NbF_7$ at $x=0.65$ recorded between different potential windows ($T=170^\circ\text{C}$; scan rate 200 mV s^{-1} ; WE-Pt disc; CE-GC; RE-Pt wire)

Figure 4.44 presents the evaluation of the reduction wave, R_1 by computer resolving into the sums of Gaussian functions.

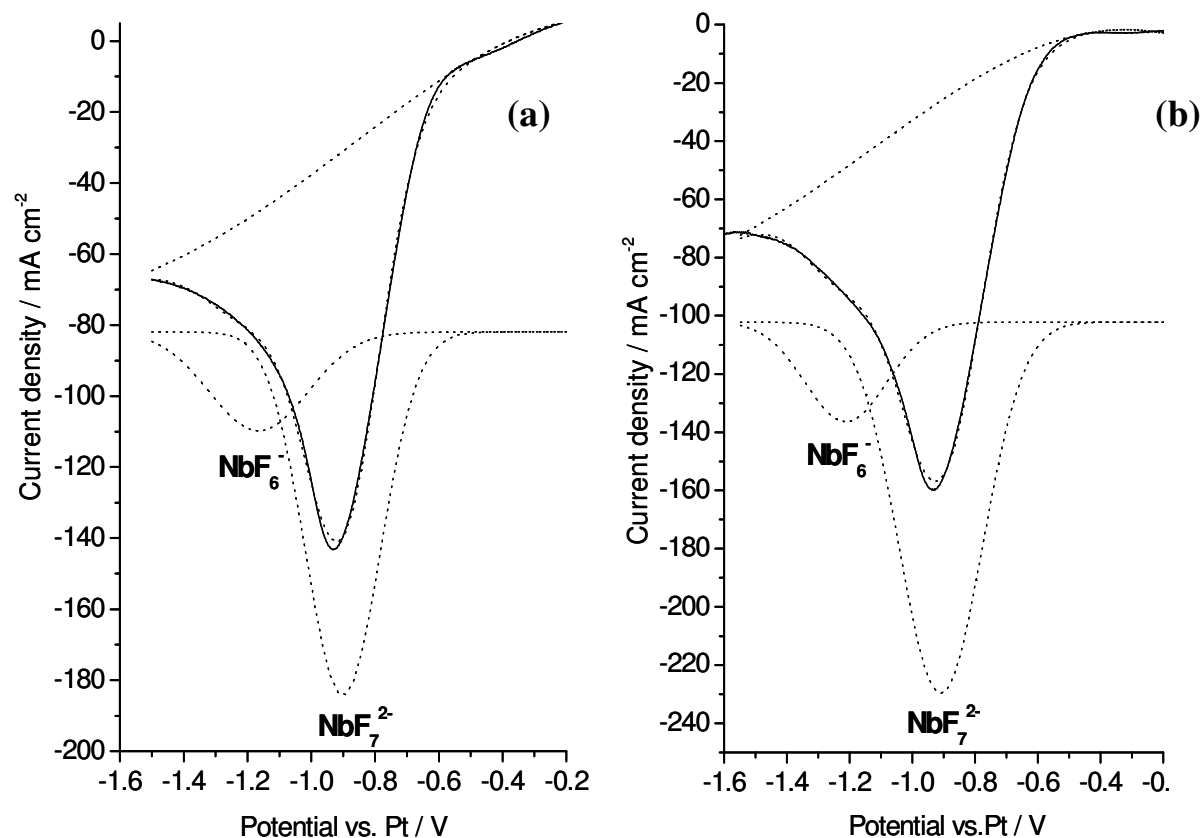


Figure 4.44. Cyclic voltammograms of ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65: (a) - Gaussian curves between potential window -1.5 V ÷ 0 V; (b) - Gaussian curves between potential window -3.0 V ÷ 3.0 V evaluated by computer resolving the reduction waves into sums of Gaussian functions

The calculations were done for cyclic voltammograms recorded between potential windows -1.5 V ÷ 0 V and -3.0 V ÷ 3.0 V. On the base of these data one may correlate the observed redox couple R_1/O_1 with the reduction of NbF_7^{2-} and NbF_6^- species at close potentials, namely: -0.90 V vs. Pt for NbF_7^{2-} and -1.16 V vs. Pt for NbF_6^- .

4.2.10. Electroplating of niobium from ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.65$ on the nickel and silver substrates

The ionic liquid $(x)\text{Pyr}_{14}\text{Cl}-(1-x)\text{K}_2\text{NbF}_7$ at $x=0.65$ was found to be the optimal composition for deposition of niobium coatings. The experiments were carried out on nickel and silver plate substrates with the areas of coverage of 0.1 cm^2 and 0.03 cm^2 , respectively. A spiral anode from pure niobium wire (diameter 1 mm, 99.8 % purity) purchased from Aldrich with an area of 0.471 cm^2 was used. Pulse interrupted and constant current deposition experiments were carried out in a two-electrode cell with temperature control. The temperature was kept 170°C and the time of electrolysis was about 1h. The distance between cathode and anode was controlled within 3-5 mm according to the cell geometry.

4.2.10.1. Pulse interrupted electroplating

A series of the pulse interrupted electroplating experiments were performed on the substrates made of nickel and the most interesting results were obtained using delay time t_{off} after deposition pulse at constant potential. In this case a short pulse t_{on} (20 sec, $E_{\text{const}} = -2.0\text{V}$) was followed by relatively long break time (40 sec.) that allowed refresh the ion concentration at the deposition interface between the pulses. The sample was characterized by SEM/EDAX in the middle of the substrate and the results are presented in *Figures 4.45., 4.46.*

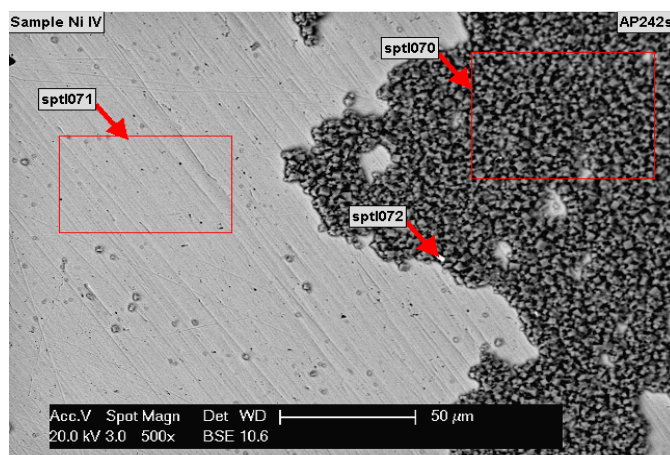


Figure 4.45. SEM micrograph of the deposit obtained during electroplating at -2.0V (t_{on} 20 sec/ t_{off} 40 sec) in the middle of the nickel substrate. Definition of spots where EDAX spectra were taken: sptl070 - deposited layer; sptl071 - uncovered nickel substrate; sptl072 - light-coloured parts within the layer

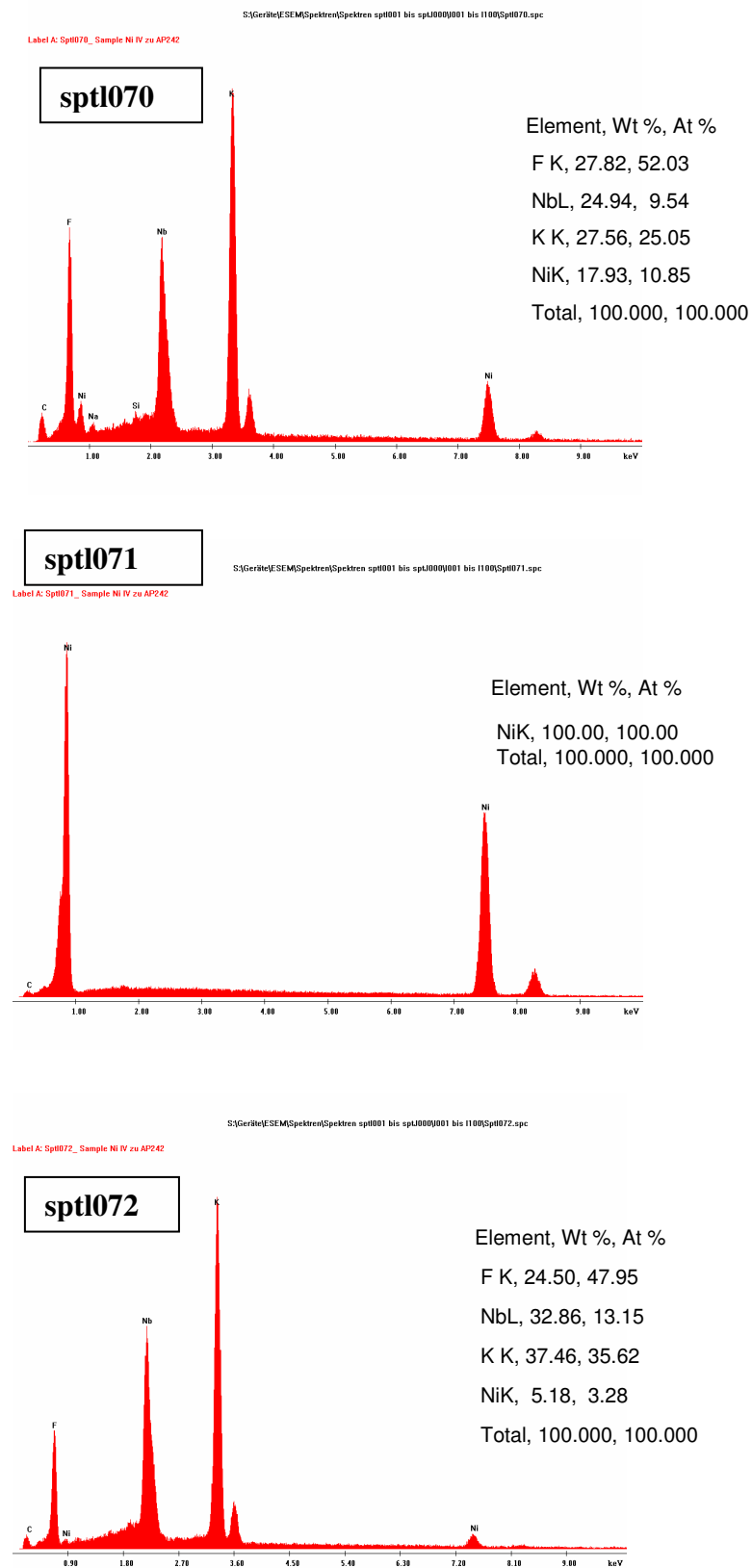


Figure 4.46. EDAX spectra of the surface in the middle of the nickel substrate of the spots specified in *Figure 4.45*.: sptl070, sptl071 and sptl072, respectively

As it can be seen from the EDAX data (Figure 4.46., spot sptl070), the deposits contain not only 9.54 atomic percent (at. %) of niobium but also K (25.05 at. %) and F (52.03 at. %). Presumably the co-adsorption of K_2NbF_7 may occur which can be adsorbed at the interface.

The similar experiments were performed on the silver substrate using pulse times t_{on} (2sec, $E_{const} = -2.0V$) and delay time t_{off} (4 sec). The sample was characterized by SEM and EDAX in the middle of the substrate and the results are presented in Figure 4.47 and Figure 4.48.

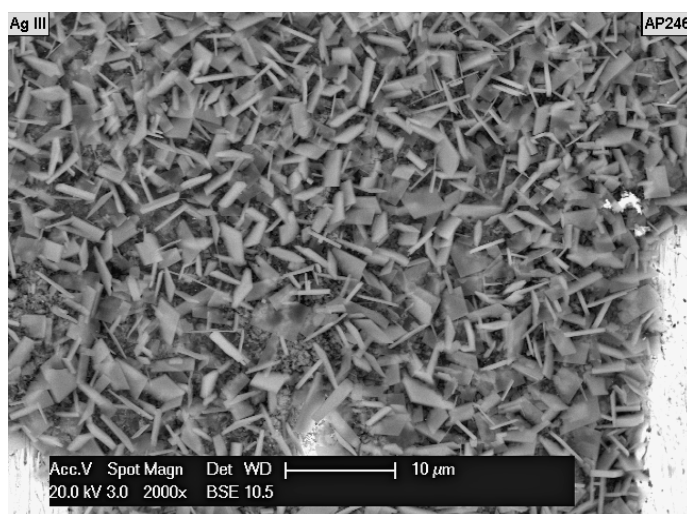


Figure 4.47. SEM micrograph of the deposit obtained during electroplating at -2.0V (t_{on} 2 sec/ t_{off} 4 sec) in the middle of the silver substrate

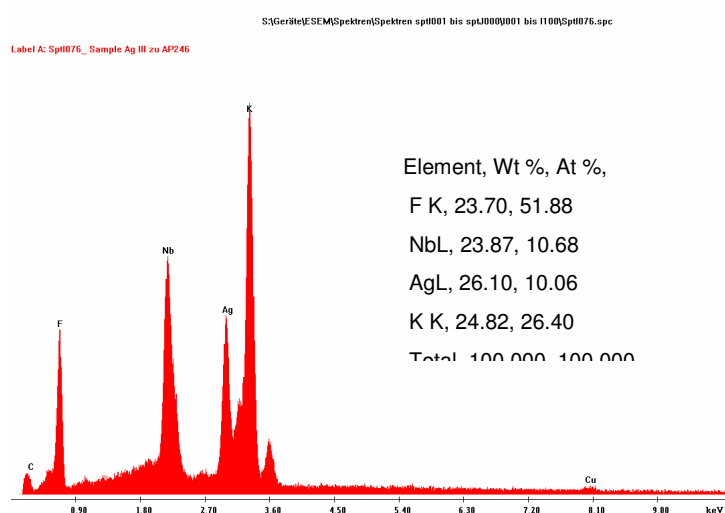


Figure 4.48. EDAX spectra of the deposit obtained during electroplating at -2.0V (t_{on} 2 sec/ t_{off} 4 sec) in the middle of the silver substrate

The sheet-like layers obtained on silver substrates were more dense and adherent than that ones obtained on nickel. But still the layer covers the substrate not uniformly. According to the EDAX spectra, the elemental composition of the deposits contain 10.68 atomic percent (at. %) of niobium as well as K (26.40 at. %) and F (51.88 at. %). The presence of Ag is attributed to the uncovered surface of the substrate.

4.2.10.2. Constant current electroplating

A series of the constant current electroplating experiments were performed on the substrates made of silver and the most interesting results were obtained after 1 hour electrolysis at current densities -50 mA cm^{-2} and -12.5 mA cm^{-2} , respectively. The samples were characterized by SEM/EDAX in the middle of the substrates and the results are presented in *Figures 4.49 - 4.51* for the experiment at -50 mA cm^{-2} and in *Figures 4.52 - 4.53* for the experiment at -12.5 mA cm^{-2} .

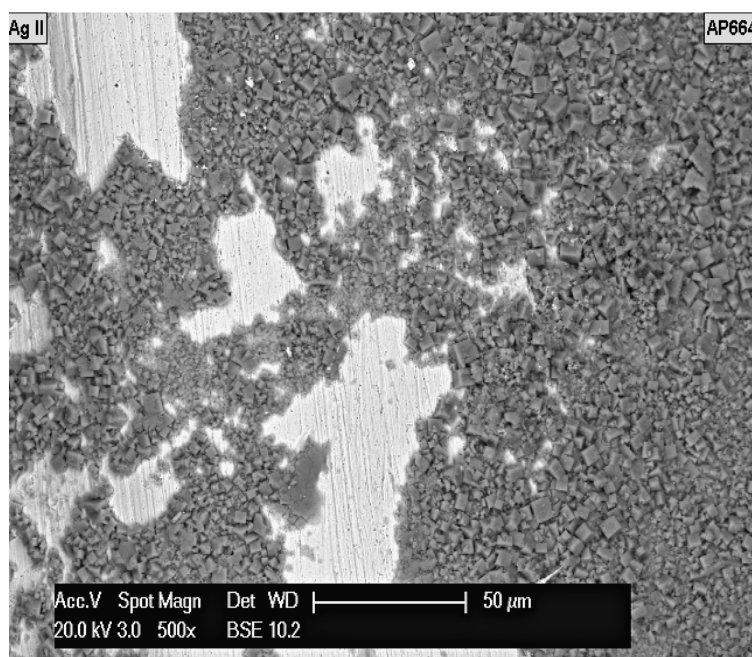


Figure 4.49. SEM micrograph of the deposit obtained during electroplating after 1 hour at -50 mA cm^{-2} in the middle of the silver substrate at magnification of 500x

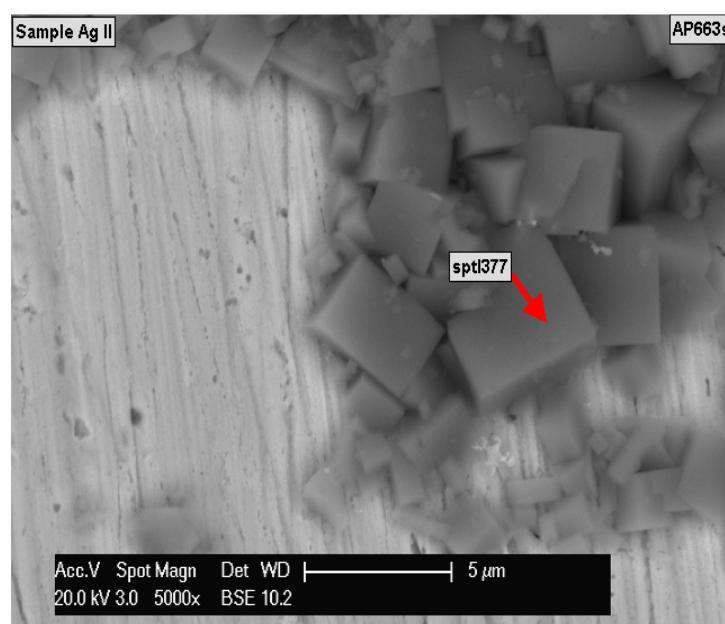


Figure 4.50. SEM micrograph of the deposit obtained during electroplating after 1 hour at -50 mA cm^{-2} in the middle of the silver substrate at magnification of 5000x. The noted spot sptl377 is on the crystal within deposited layer where EDAX spectra was taken

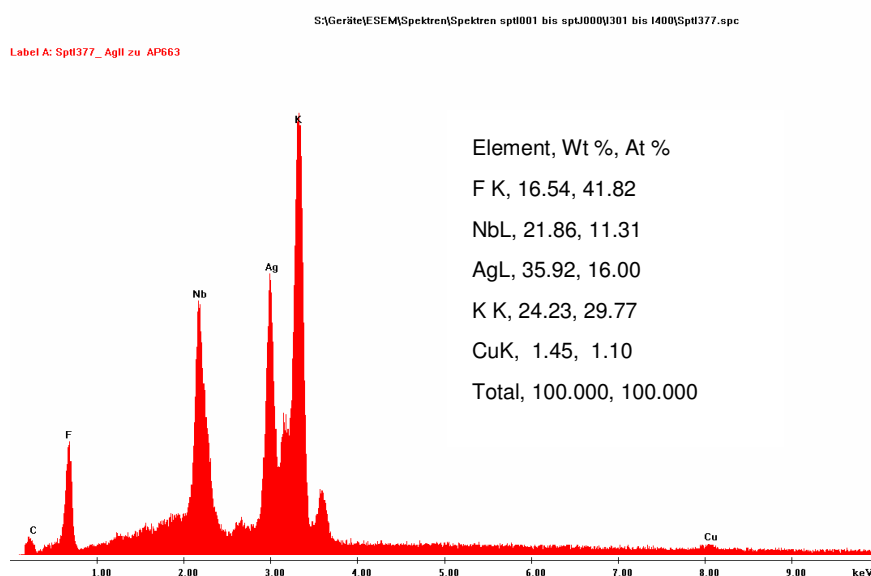


Figure 4.51. EDAX spectra of the deposit obtained during electroplating after 1 hour at -50 mA cm^{-2} in the middle of the silver substrate of the spot sptl377 specified in *Figure 4.50*.

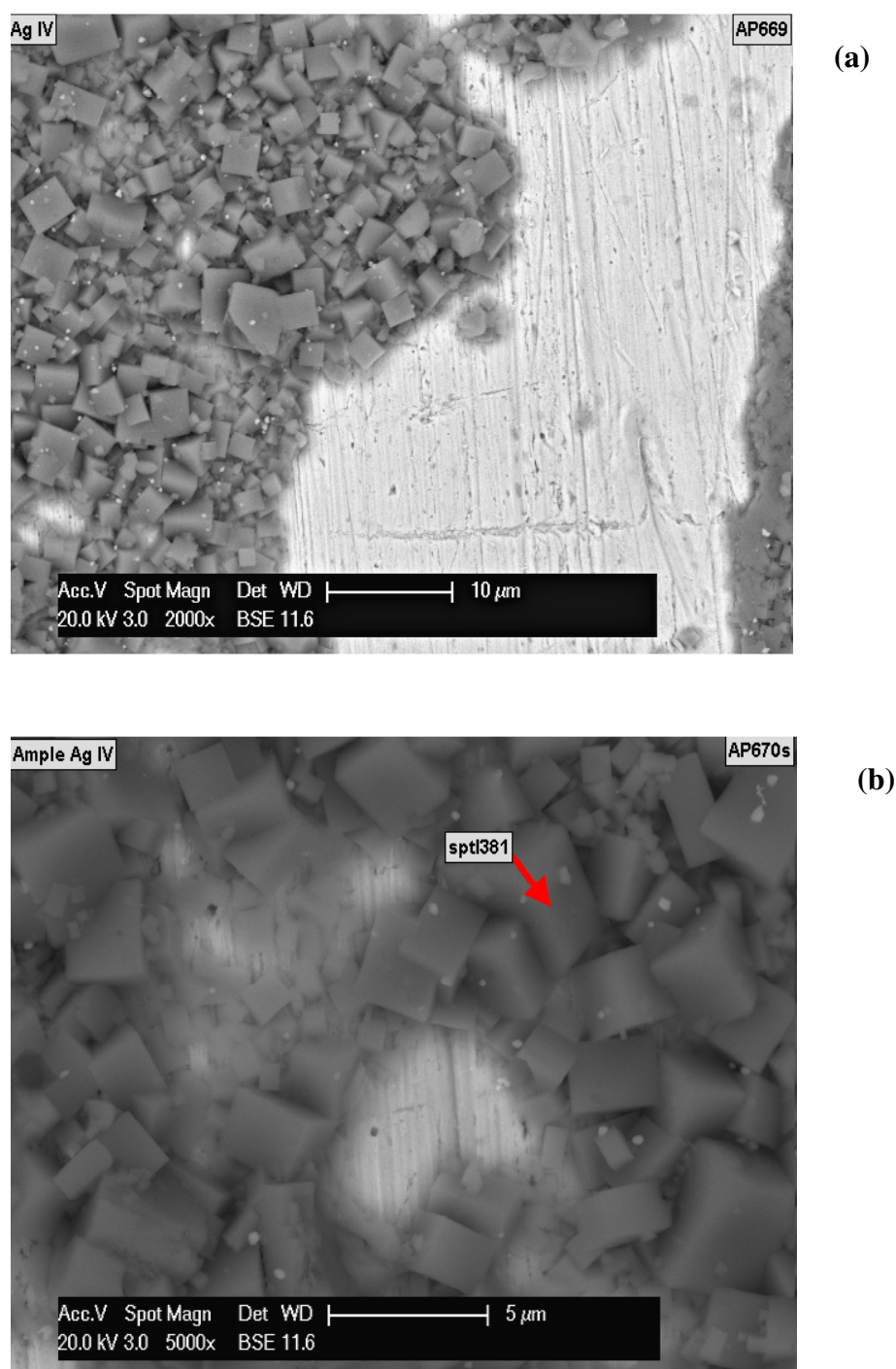


Figure 4.52. SEM micrographs of the deposit obtained during electroplating after 1 hour at - 12.5 mA cm^{-2} in the middle of the silver substrate (at magnification of 2000x **(a)** and 5000x **(b)**, respectively). The noted spot spt1381 is on the crystal within deposited layer where EDAX spectra was taken

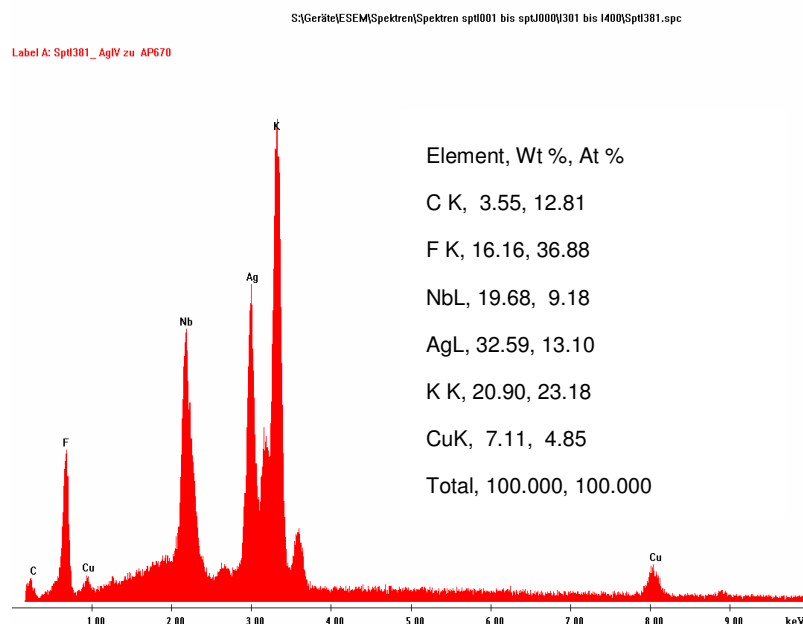


Figure 4.53. EDAX spectra of coating obtained during electroplating at -12.5 mA cm^{-2} in the middle of the silver substrate at spot spt1381 specified in *Figure 4.52*.

One can see from *Figure 4.49.* and *Figure 4.52. a* that the surface of substrates after electrolysis at -50 mA cm^{-2} and -12.5 mA cm^{-2} is covered by irregular and inhomogeneous layer. The shape of the crystals in both cases is quite similar and close to cubic form plates. The results of EDAX (*Figures 4.51., 4.53.*) demonstrate that the deposits obtained at different current densities (at -50 mA cm^{-2} and -12.5 mA cm^{-2}) contain approximately the equal amount of niobium (11.31 and 9.18 at. %) as well as F (41.82 and 36.88 at. %) and K (29.77 and 23.18 at. %).

An overview of the main results of the electroplating experiments on the basis of the SEM pictures is given in *Figure 4.54*. For illustration purposes, the fragments of the SEM micrographs of the deposits obtained during electroplating under different conditions are presented at the same magnification. The equal average size of the crystals is now evident. The corresponding EDAX results are collected in *Table 4.8*.

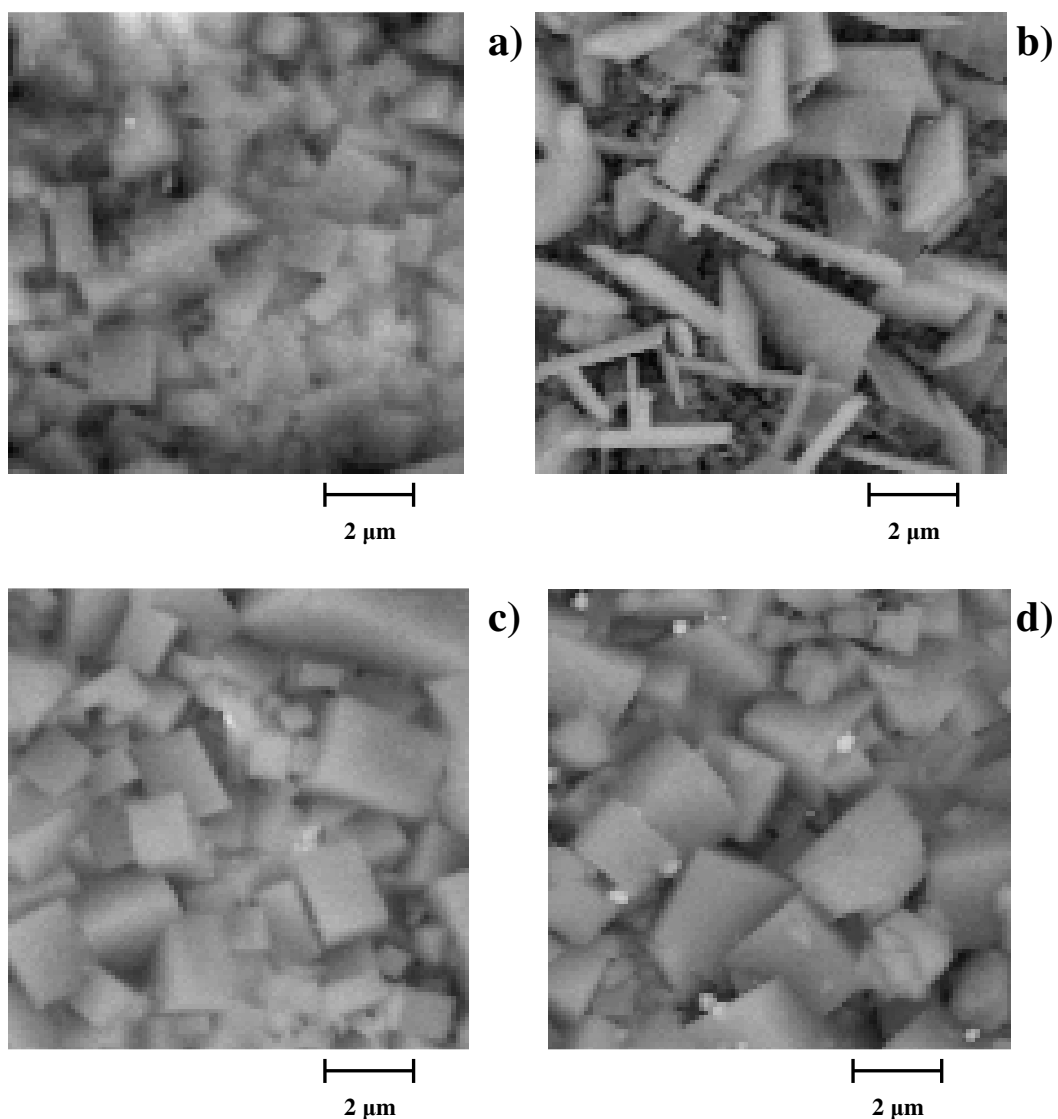


Figure 4.54. SEM micrographs corresponding to electroplating experiments as specified in *Table 4.8*. Samples after pulse interrupted electroplating: **(a)** - Ni substrate (-2.0V , t_{on} 20 sec/ t_{off} 40 sec); **(b)** - Ag substrate (-2.0V , t_{on} 2 sec/ t_{off} 4 sec), and samples after constant current electroplating: **(c)** - Ag substrate (-50mA cm^{-2}); **(d)** - Ag substrate (-12.5mA cm^{-2})

Table 4.8. Experimental conditions of electroplating measurements in ionic liquid (x)Py₁₄Cl-(1-x)K₂NbF₇ at x=0.65 on Ni and Ag substrates and corresponding EDAX results of the composition of the deposits

Pulse interrupted electroplating		Constant current electroplating	
(a) Ni substrate	(b) Ag substrate	(c) Ag substrate	(d) Ag substrate
$E_{\text{const}} = -2.0\text{V}$ $t_{\text{on}} (20\text{sec})$ $t_{\text{off}} (40 \text{ sec})$ Duration=78min	$E_{\text{const}} = -2.0\text{V}$ $t_{\text{on}} (2\text{sec})$ $t_{\text{off}} (4 \text{ sec})$ Duration=100min	$i = -50\text{mA cm}^{-2}$ Duration=60min	$i = -12.5\text{mA cm}^{-2}$ Duration=60min
At % F – 52.03 Nb – 9.54 K – 25.05 O- no	At % F – 51.88 Nb – 10.68 K – 26.40 O- no	At % F – 41.82 Nb – 11.31 K – 29.77 O- no	At % F – 36.88 Nb – 9.18 K – 23.18 O- no

4.2.11. Conclusions

Focusing on the mechanism of electrochemical reduction of niobium(V) and on the deposition of niobium metal from ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇, the following observations of this study are of the particular interest.

- In basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at $x=0.65$; 0.60, and 0.40, the equilibrium between the electrochemically active species, NbF₇²⁻ and NbF₆⁻ was estimated on the basis of *in situ* Raman spectroscopic data at 170°C;
- The specific feature of basic ionic liquid at $x\approx 0.80$ is that the spectral characteristics of the same sample are changed depending on the time of storage. NbF₇²⁻ and NbF₆⁻ ions are present in fresh sample while only [NbF₆]⁻ species were identified in 2 days by means of Raman spectroscopy. The plausible explanation may consist in the loose of the identity of NbF₇²⁻ ions most probably due to the formation of different ionic pairs and more complicated aggregates which are not detectable by spectroscopic methods;
- As the co-existence of NbF₆⁻ and NbF₇²⁻ species was confirmed in both basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at 160-170°C, the electrochemical characterization was performed in ionic liquid at $x=0.65$;
- A pronounced reduction wave is observed at -0.9 V indicating the reduction reaction Nb(V) to Nb(IV). The characteristics of the corresponding voltammograms are not consistent with the diagnostics of a simple reversible reaction but suggest the reduction of both electrochemically active species, NbF₇²⁻ and NbF₆⁻ at the close potentials around -0.9 V;
- At the potential below -2.0 V, a strong decrease of cathodic currents is apparent which may be correlated with niobium metal deposition by analogy with high temperature molten salts electrolytes;
- Electroplating experiments were performed from ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at $x=0.65$ on nickel and silver plate substrates at 170°C using the pulse interrupted and constant current techniques;
- EDAX measurements unambiguously show the electrodeposition of K₂NbF₇ at a potential of -2.0 V at 170°C from the ionic liquid (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at $x=0.65$. Corresponding SEM micrographs exhibit well defined and different crystal structures at the interfaces of the ionic liquid melts and substrates like Ni or Ag. One may assume that niobium metal electrodeposition in these ionic liquid mixture is presumably expected at potentials more negative of -2.0 V.

PART 5. SUMMARY

The synthesis of novel ionic liquids consisting of 1-butyl-1-methylpyrrolidinium chloride (Pyr₁₄Cl) as an organic part and the salts of niobium(V), namely NbCl₅ and K₂NbF₇ as an inorganic part at various mole fractions of the components was performed. The mixtures (x)Pyr₁₄Cl-(1-x)NbCl₅ form orange and brown liquids in a wide range of compositions $x=0.85\div0.20$ at the temperatures 140-170°C. The mixtures (x)Pyr₁₄Cl-(1-x)K₂NbF₇ form milky-white opaque liquids at ~170-180°C in basic-neutral range of compositions ($x=0.80\div0.50$). Acidic ionic liquids ($x=0.40\div0.20$) form opaque gel-like mixtures at ~190°C.

Ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅

The 1-butyl-1-methylpyrrolidinium chloride was used as a model system with a simple Cl⁻ anion which potentially may form ionic liquids with NbCl₅ that resemble the high temperature alkali chloride melts. According to the Raman data, in basic ionic liquids (x)Pyr₁₄Cl-(1-x)NbCl₅ at $x=0.85-0.80$, the self-reduction of niobium(V) to tetravalent state was observed and octahedral species NbCl₆⁻ and NbCl₆²⁻ were identified. In the range of compositions $x=0.85-0.50$, niobium(V) exists as the octahedral complexes NbCl₆⁻. In acidic mixtures at $x=0.45-0.20$, the niobium(V) species are present in the form of Nb₂Cl₁₀ and Nb₂Cl₁₁⁻. Because of the different structure and composition of electrochemically active species (ECAS) of niobium(V) identified in basic and acidic ionic liquids, three systems were chosen for electrochemical measurements: at $x=0.80$, 0.60, and 0.40.

For the first time the combination of Raman spectroscopic measurements with electrochemical studies was used to get a detailed insight in the mechanism of electrochemical reduction of Nb(V) in ionic liquid electrolyte (x)Pyr₁₄Cl-(1-x)NbCl₅. The range of operating temperatures was found to be rather limited (135-145°C) due to the high viscosity of the ionic liquid at lower temperatures and its starting decomposition at elevated temperatures.

In basic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at $x=0.80$ the reduction of niobium(V) occur in three steps: the first one is a one electron transfer of minor species NbCl₆⁻ ($\text{Nb}^{5+} + 1\text{e}^- \rightarrow \text{Nb}^{4+}$) at -0.02 V vs. Pt ref., the second one is a one electron transfer of the main species NbCl₆²⁻ ($\text{Nb}^{4+} + \text{e}^- \rightarrow \text{Nb}^{3+}$) at -1.70 V vs. Pt ref., and presumably the further reduction of Nb³⁺ to metallic niobium at potentials lower than -2.10 V vs. Pt ref.

In acidic melts NbCl₆⁻ and Nb₂Cl₁₁⁻ species coexist and the electrochemical reduction mechanism now is: $\text{Nb}^{5+} \rightarrow \text{Nb}^{4+} \rightarrow \text{Nb}^{3+}$. In the acidic ionic liquid (x)Pyr₁₄Cl-(1-x)NbCl₅ at

x=0.40 the reduction of niobium(V) to niobium(III) occur in two steps: the first is a one electron transfer of NbCl_6^- species ($\text{Nb}^{5+} + 1e^- \rightarrow \text{Nb}^{4+}$) at -0.45 V vs. Pt ref., the second is a two electrons transfer of $\text{Nb}_2\text{Cl}_{11}^-$ species ($\text{Nb}^{5+} + 1e^- \rightarrow \text{Nb}^{4+}$ and $\text{Nb}^{4+} + 1e^- \rightarrow \text{Nb}^{3+}$) at -1.12 V and -1.27 V vs. Pt ref., respectively.

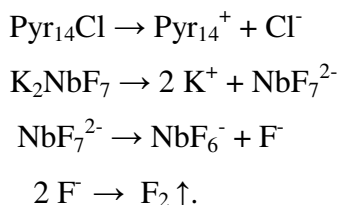
The anodic dissolution of niobium was investigated in the most explored system - the basic ionic liquid (x) Pyr_{14}Cl -(1-x) NbCl_5 at x=0.80. Supplementary electrochemical and spectroscopic experiments were performed in ionic liquids (x) Pyr_{14}Cl -(1-x) NbCl_5 at x=0.80 and 0.60 with chemical and electrochemical dissolution of niobium. The presence of niobium species in lower oxidation states in the solutions where niobium ions were introduced via electrochemical dissolution of niobium metal electrode was confirmed by Raman spectroscopic data.

The electrolyte at x=0.80 where Nb(V) and Nb(IV) species were identified by means of Raman spectroscopy and the self-reduction $\text{Nb(V)} \rightarrow \text{Nb(IV)}$ was confirmed earlier, demonstrates the shift of this equilibrium towards formation of Nb(IV) when niobium soluble electrode was used. This ionic liquid at molar ratio of Pyr_{14}Cl x=0.80 was considered as the most preferable for the electrodeposition of metallic niobium.

The influence of alkali metal halides, namely KF, RbF and CsF on the reduction of niobium(V) in ionic liquid (x) Pyr_{14}Cl -(1-x) NbCl_5 at various molar ratios for the sake of electrodeposition of niobium was investigated. A beneficial effect of the additive RbF was observed and the ionic liquid Pyr_{14}Cl - NbCl_5 -RbF at molar ratio of components 60/30/10 mole %, respectively was found to be the most promising candidate for electrochemical deposition of niobium. The plate-like oxygen containing deposits with 8.57 atomic percent of niobium were obtained after 1 hour electrolysis out of ionic liquid Pyr_{14}Cl - NbCl_5 -RbF (60/30/10) on the nickel substrate. As there is no pure niobium was deposited, it can be concluded that in such ionic liquids under these conditions the metallic niobium is not formed during the electrolysis. A lot of work should be done to investigate the optimal parameters and to estimate the factors which are restricted the deposition processes. Although we did not succeed to characterize metallic niobium deposits with these ionic liquids, the main issue of this study was to elucidate the reduction mechanism which finally may lead to niobium deposition.

Ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇

The structure and composition of niobium(V) species in basic and acidic ionic liquids (x)1-butyl-1-methyl-pyrrolidinium chloride-(1-x)K₂NbF₇ (x=0.80-0.20) was investigated over the temperature range 20-200°C by means of *in situ* Raman spectroscopy and FTIR spectroscopy with respect to the electrochemical deposition of niobium. These ionic liquids can be classified as “the mixed chloride-fluoride electrolytes” by analogy with high temperature molten salts. In the mixtures (x)Pyr₁₄Cl-(1-x)K₂NbF₇, the formation of ionic liquids is accompanied by more complicated process of the dissociation of K₂NbF₇ and leads to the formation of ionic liquids which possess the properties of electrolytes in basic and acidic range of concentration. In basic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇ (x>0.50), Pyr₁₄Cl is the solvent for K₂NbF₇. In acidic ionic (x<0.50), the molecule of Pyr₁₄Cl are introduced in the crystal lattice of K₂NbF₇. The following schemes of complex formation – dissociation might be considered:



Even in the excess of Cl⁻ anions, the formation of mixed fluoride-chloride complexes seems unlikely. On the basis of *in situ* Raman spectroscopic data, the co-existence of two species of niobium(V), NbF₆⁻ and NbF₇²⁻, was confirmed in both basic and acidic ionic liquids (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at operating temperatures of 160-170°C. As the set of electrochemically active species was found to be similar in the basic and acidic range of compositions, the mechanism of electrochemical reduction of niobium(V) was investigated in the basic mixture at x=0.65.

Diagnostic tests for reversible electron transfer made on the base of cyclic voltamograms recorded for mixture (x)Pyr₁₄Cl-(1-x)K₂NbF₇ at x=0.65 indicate that the redox process R₁/O₁ at -0.90 V ÷ -0.66 V (vs. Pt ref.) is not a simple reversible one. Possibly, two electrochemical active species of niobium(V), NbF₇²⁻ and NbF₆⁻, participate in the electrochemical reduction at close potentials. The strong decrease of cathodic currents below -2.0 V might be indicative of niobium metal deposition. By analogy with high temperature investigations in alkali halide melts the potential difference of about -1.0 V relative to the Nb(V)-Nb(IV) redox potential suggests that niobium metal deposition should set in below -

2.0 V in the ionic liquid of interest here. In how far it is overlapped by potassium deposition is unclear.

A series of the pulse interrupted and constant current deposition experiments were performed on the substrates made of nickel and silver. According to the EDAX spectra, the elemental composition of the deposits contain from 9.18 up to 11.31 atomic percent (at. %) of niobium as well as K ($23.18 \div 29.77$ at. %) and F ($36.88 \div 52.03$ at. %), which presumably indicate the co-adsorption of K_2NbF_7 . Corresponding SEM micrographs exhibit well defined and different crystal structures at the interfaces of the ionic liquid melts and substrates like nickel or silver. One may assume that niobium metal electrodeposition in these ionic liquid mixture is presumably expected at potentials more negative of -2.0 V.

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Publications

Articles

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2. O.B. Babushkina, E.O. Lomako, W. Freyland., "Spectroscopy and electrochemistry of niobium in basic and acidic pyrrolidinium based ionic liquids. Part II: 1-Butyl-1-methylpyrrolidinium chloride with K₂NbF₇", *submitted to Electrochim. Acta*

Proceedings

O.B.Babushkina, E.O.Lomako, J.Wehr, O.Rohr, "Electrodeposition of Aluminium from Ionic Liquids", 9th International Symposium on Molten Salts Chemistry and Technology, Trondheim, Norway, 5-9 June, 2011, Extended Abstract

Participation in Conferences (Poster and Oral Presentations)

1. E.Lomako, O.Babushkina

"Electrochemistry and Spectroscopy of Niobium(V) in Ionic Liquids"

14. Österreichische Chemietage / 14th Austrian Chemistry Days,
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2. E.Lomako, O.Babushkina

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European Congress and Exhibition on Advanced Materials (EUROMAT) 2011,
September 12-15, 2011, Montpellier, France

3. O.B.Babushkina, E.O.Lomako, J.Wehr, O.Rohr

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4. E. Lomako, O. Babushkina

"Electrochemistry of Nb(V) in Basic and Acidic Ionic Liquids Based on 1-Butyl-1-Methylpyrrolidinium Chloride"

The 61th Annual meeting of the International Society of Electrochemistry,
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5. E.Lomako and O.Babushkina

"Reduction Products of Niobium(V) in Ionic Liquid 1-Butyl-1-Methylpyrrolidinium Chloride- NbCl₅"

216th ECS Meeting,
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6. Babushkina, Y.Andryiko, E.Lomako

"Inter-Ionic Interaction in Ionic Liquids (x)TiF₄-(1-x)1-Butyl-2,3-Methylimidazolium Tetrafluoroborate. Raman and FTIR Spectroscopic Study"

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7. O.Babushkina and E.Lomako

"Raman Spectroscopic Studies of Niobium(V) in Pyrrolidinium Based Ionic Liquids in Solid and Molten States"

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8. O.B.Babushkina, E.O.Lomako, S.Ekres, G.E.Nauer

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9. O.B.Babushkina, E.O.Lomako, G.E.Nauer

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