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in

“Surface Treatments for Industrial Applications”

**Attempts for the electrodeposition of niobium from ionic
liquids**

Supervisor: Prof. V. Palmieri

Co-Supervisor: Dr. V. Rampazzo

*Student: Dott. Chirkov
Dmytro Vasiliovich*

Matr. N°: 938772

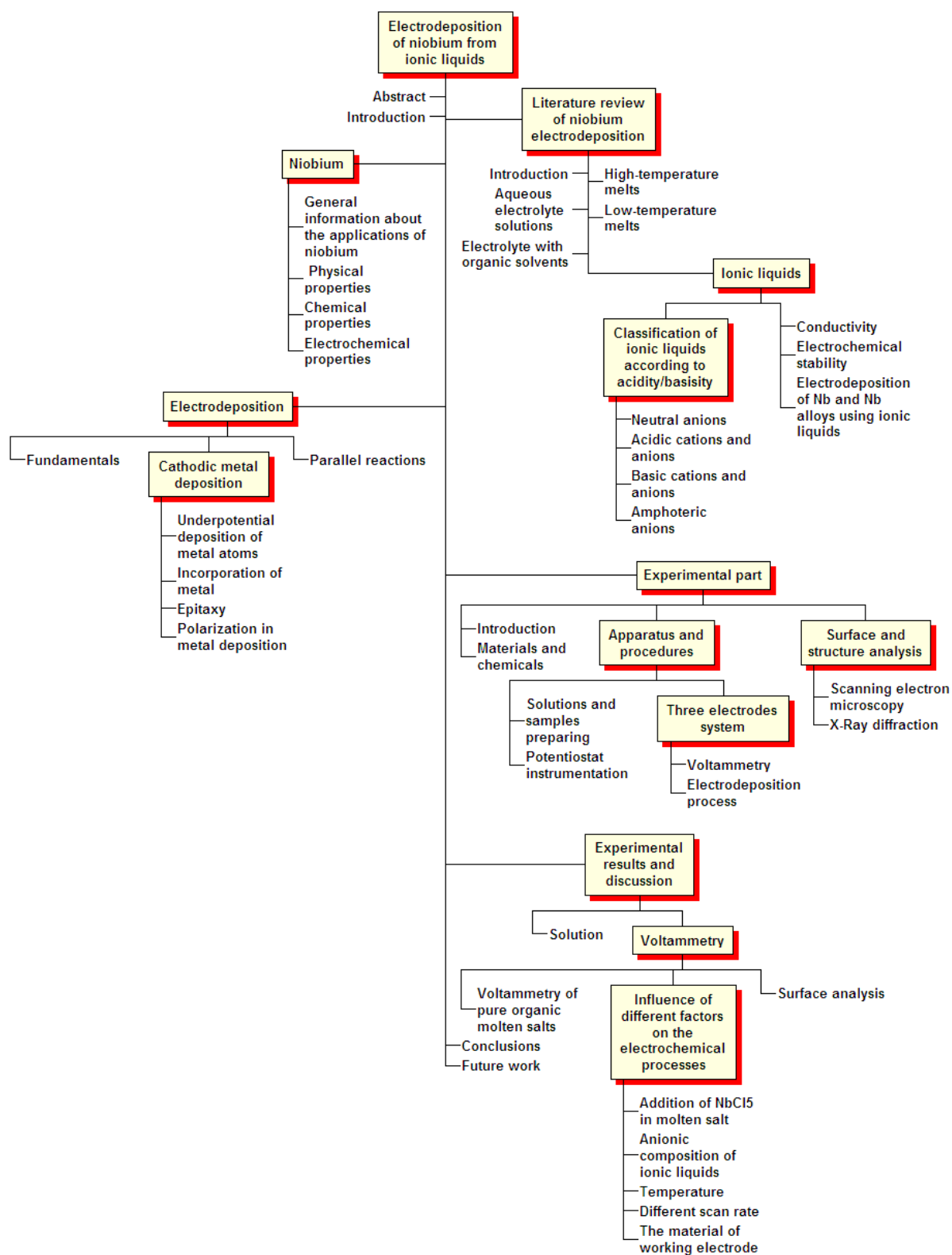
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Scheme of the thesis



Abstract

The main aim of this work is try to electrodeposit metallic niobium films from room-temperature ionic liquids.

Nowadays electrochemical surface treatment is one of the most used approaches in industry.

Aqueous solutions has been the most widely used process mainly because of advantages such us low cost, non-flammability, high solubility of electrolytes, high conductivities resulting in low ohmic losses, high solubility of metal salts and high rates of mass transfer. However, despite these advantages there are several limitations in using aqueous solutions such as limited potential windows, gas evolution processes that can result in hydrogen embrittlement, passivation of substrates, electrodes and deposits, and the necessity for hazardous complex agents such as cyanide, causing environmental contamination. These are the reasons why new non-aqueous solutions to electrodeposit niobium have been researched.

One of the main limitations in using aqueous solutions is their narrow electrochemical window. The major reason for carrying out electrodeposition in non-aqueous electrolytes (such as conventional organic solvents, molten salts or ionic liquids) is water and air stability and the wide electrochemical window of these media.

Alternatively, also high temperature molten salts have been used extensively for niobium electrodeposition. They have wide potential windows, high conductivities and high solubility for metal salts. In fact, they have most of the advantages of aqueous solutions and overcome most of the limitations of aqueous solutions, but their one major limitation is the very high temperature (more than 750°C).

Therefore, the alternative to high temperature molten salts was an ionic substance that melts at a low temperature. Over the last few decades, room temperature ionic liquids have been widely studied in various scientific fields due to their interesting properties, such as negligible vapour pressures, high chemical and thermal stability, acceptable intrinsic ionic conductivity and wide potential window.

Ionic liquids are molten salts with melting points below 100°C and they consist entirely of cations and anions. The development of ionic liquids, especially air and water stable types, has attracted extensive attention since they have outstanding physical properties.

The aim of this work will be the analysis of available literature data in order to have precise knowledge about niobium behavior in the different electrolytes and to get new information about possible electrolytes based on ionic liquids.

Introduction

0.1. Niobium

0.1.1. General information about the applications of niobium

Niobium (in the older literature is also known as Columbium (Cb) is the 41st element of the periodic table. It was discovered in 1801 by the English chemist Charles Hatchett. One year later, a Swedish chemist, Anders Ekeberg, announced his discovery of tantalum. Both tantalum and niobium were discovered in the form of oxides. It took about 65 years until an effective method for the separation of tantalum and niobium was found by Jean Charles Galissard de Marignac, in 1866 [1]. Niobium is rare element. The content of niobium in the Earth's crust is 1×10^{-3} wt.% [2]. The most important source of niobium is columbite – $(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$.

Niobium is used widely, in the form of metals and alloys, in the process industry, vacuum techniques, surgical devices, and the automotive industry [3; 4].

However, the vast majority of Nb reduced from raw ores each year is used as an alloying element in steels. Niobium additives are used to stabilize and improve modern stainless steels [5; 6], and superalloys containing tantalum and niobium are successfully applied in gas turbine engines and in the aerospace industry [7; 8; 9].

Niobium nitride (NbN), which becomes a superconductor at low temperatures are used in detectors for infrared light.

The compounds niobium-germanium (Nb_3Ge) and niobium-tin (Nb_3Sn), as well as the niobium-titanium alloy, which display superconductivity at relatively high temperatures, are used as a type II superconductor wire for superconducting magnets in special applications [10; 11].

Niobium-titanium alloys are used for superconducting magnets in magnetic resonance imaging equipment used for the detection of abnormalities in soft tissue.

Niobium is added, in the form of carbides, to cemented carbide compositions used in the production of cutting tools. Pure oxides are widely used in the optical industry as additives and deposits, and in organic synthesis processes as catalysts and promoters [12; 13].

0.1.2. Physical properties

Niobium is steel-grey metal with the body centered cubic (bcc) crystal system. It is a refractory metal because of very high melting point. Pure metal is plastic and could be cold rolled to thin sheet without intermediate annealing [14].

In addition to a high melting point, niobium offers lower density and low thermal neutron cross-section compared to other refractory metals, which makes niobium useful in atomic reactors. In addition to its small capture cross-section for fast neutrons, niobium is highly recommended in nuclear reactors because of its good high temperature creep strength, its resistance to corrosion by liquid sodium-potassium alloys, and its outstanding compatibility with nuclear fuels. However, because of the poor oxidation resistance of high temperatures of niobium-base alloys, they must be coated before use in nuclear environments. Therefore, a niobium 1% zirconium alloy is used as a construction material in nuclear engineering, where its low neutron absorption coefficients, along with its good resistance to liquid sodium or lithium are utilized [15]. The most important physical properties of niobium are collected in Table 0.1:

Atomic number	41
Atomic weight	92,906
Density, g/cm ³	8,57
Atomic radius, nm	0,146
Melting point, °C	2470±10
Boiling point, °C	~4744
Valence Electrons	4d ⁴ 5s ¹
Specific heat capacity (25°C), J/mol·K	24,60
Thermal conductivity (300K), W/m·K	53,7
Thermal expansion, µm/(m·K)	7,3

Table 0.1: *Physical properties of niobium*

Typical property of niobium is possibility to absorb gases – hydrogen, oxygen, nitrogen. Low impurity of these elements strongly influence on mechanical and electrical properties of metal.

Superconductivity is a phenomenon observed in some materials: the disappearance of the electrical resistivity at temperatures approaching 0K. The temperature below which materials become superconducting is defined as the critical temperature, T_c . Niobium becomes a superconductor at low temperatures. At atmospheric pressure, it has the highest

critical temperature of the elemental superconductors: 9,2K. Niobium has the largest magnetic penetration depth of any element. In addition, it is one of the three elemental Type II superconductors, along with vanadium and technetium. The superconductive properties are strongly dependent on the purity of the niobium metal. When very pure, it is comparatively soft and ductile, but impurities make it harder.

In 1973 the alloy Nb₃Ge was found to have a $T_c = 23\text{K}$, which remained the highest attainable critical temperature until 1986.

0.1.3. Chemical properties

At normal temperature niobium is stable in contact with air. The beginning of oxidation (tarnish) is observed during the heating to 200-300°C. Higher 500°C fast oxidation occurs with formation of Nb₂O₅ [14].

Niobium oxides dissolve very slowly in HF solutions. Because of oxide films on the surface niobium has an excellent corrosion resistance in mineral (hydrochloric, sulfuric, nitric, phosphoric) and organic acids all concentrations at 10-150°C. Metal slowly dissolves in hydrofluoric acid and intensively - in mixture of hydrofluoric and nitric acids. It also dissolves in hot solutions of sodium and potassium hydroxides.

Niobium reacts with most nonmetals at high temperatures: it reacts with fluorine at room temperature, with chlorine and hydrogen at 200°C, and with nitrogen at 400°C, giving products that are frequently interstitial and nonstoichiometric [16].

Niobium is able to form oxides with the oxidation states +5 (Nb₂O₅), +4 (NbO₂) and +3 (Nb₂O₃) [17], as well as with the rarer oxidation state +2 (NbO) [18]. The most stable oxidation state is +5, the pentoxide which, along with the dark green non-stoichiometric dioxide, is the most common of the oxides. Niobium pentoxide is used mainly in the production of capacitors, optical glass, and as starting material for several niobium compounds [19]. The compounds are created by dissolving the pentoxide in basic hydroxide solutions or by melting it in another metal oxide. Examples are lithium niobate (LiNbO₃) and lanthanum niobate (LaNbO₄). In the lithium niobate, the niobate ion NbO₃⁻ is not alone but part of a trigonally distorted perovskite-like structure, while the lanthanum niobate contains lone NbO₄³⁻ ions [17].

Lithium niobate, which is a ferroelectric, is used extensively in mobile telephones and optical modulators, and for the manufacture of surface acoustic wave devices. It belongs to the ABO₃ structure ferroelectrics like lithium tantalate and barium titanate [20].

Niobium forms halogen compounds in the oxidation states of +5, +4, and +3 of the type NbX_5 , NbX_4 , and NbX_3 , although multi-core complexes and substoichiometric compounds are also formed [17; 21]. Niobium pentafluoride (NbF_5) is a white solid with a melting point of 79°C and niobium pentachloride (NbCl_5) is a yellowish-white solid with a melting point of $203,4^\circ\text{C}$. Both are hydrolyzed by water and react with additional niobium at elevated temperatures by forming the black and highly hygroscopic niobium tetrafluoride (NbF_4) and niobium tetrachloride (NbCl_4). While the trihalogen compounds can be obtained by reduction of the pentahalogenes with hydrogen, the dihalogen compounds do not exist [17].

Spectroscopically, the monochloride (NbCl) has been observed at high temperatures [22]. The fluorides of niobium can be used after its separation from tantalum [23]. The niobium pentachloride is used in organic chemistry as a Lewis acid in activating alkenes for the carbonylene reaction and the Diels-Alder reaction. The pentachloride is also used to generate the organometallic compound niobocene dichloride ($(\text{C}_5\text{H}_5)_2\text{NbCl}_2$), which in turn is used as a starting material for other organoniobium compounds [24].

Niobium sulphide as well as a few interstitial compounds of niobium with silicon are also known.

0.1.4. Electrochemical properties

Potential-pH plots are known as Pourbaix diagrams since they were first made by Pourbaix in 1938 [25]. A compilation of these diagrams is available in the *Atlas of Electrochemical Equilibria in Aqueous Solutions* [26].

In practice, Pourbaix diagrams are suitable for studies of corrosion, electrowinning, electroplating, hydrometallurgy, electrolysis, electrical cells, and water treatment since they are electrochemical maps indicating the domain of stability of ions, oxides and hydroxides.

This map provides the oxidizing power in an electrochemical field measured as potential and the acidity and alkalinity of species measured as pH. Thus, any reaction involving hydroxyl (OH^-) ions should be written in terms of H^+ ion concentration, which in turn is converted into pH. Besides the possible reactions that may occur in an electrochemical system, a simplified Pourbaix diagram gives important areas for designing and analyzing electrochemical systems. These areas are known as corrosion, passivation and immunity.

Figure 0.1 shows a schematic Nb- H_2O Pourbaix diagram, which includes the water and oxygen lines for comparison purposes. The construction of the diagram consists of determining the potential E using the Nernst equation, and the pH using known equilibrium constant K .

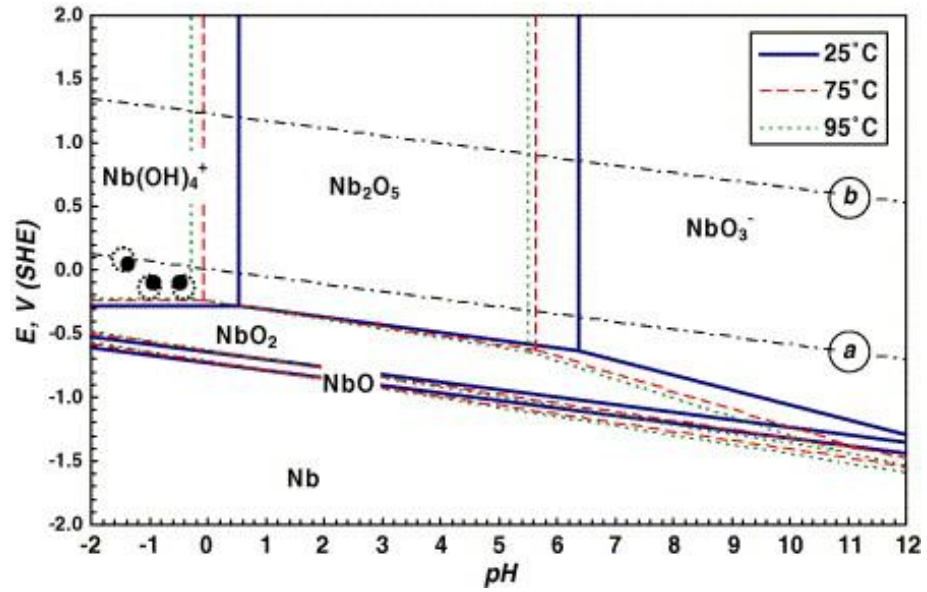


Figure 0.1: Pourbaix diagram for system Nb-H₂O

N ^o	Reaction	Line
1	$\text{Nb} + \text{H}_2\text{O} \leftrightarrow \text{NbO} + 2\text{H}^+ + 2\text{e}^-$	$E = -0,733 - 0,0591 \cdot \text{pH}$
2	$\text{NbO} + \text{H}_2\text{O} \leftrightarrow \text{NbO}_2 + 2\text{H}^+ + 2\text{e}^-$	$E = -0,625 - 0,0591 \cdot \text{pH}$
3	$2\text{NbO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Nb}_2\text{O}_5 + 2\text{H}^+ + 2\text{e}^-$	$E = -0,289 - 0,0591 \cdot \text{pH}$
a	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$E = -0,0591 \cdot \text{pH}$
b	$4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$	$E = 1,23 - 0,0591 \cdot \text{pH}$

Table 0.2: Reactions of equilibrium in Nb-H₂O system

1. Electrodeposition

1.1. Fundamentals

Electrochemistry covers all phenomena in which a chemical change is the result of electric forces and, vice versa, where an electric force is generated by chemical processes [27]. It includes the properties and behavior of electrolytic conductors in liquid or solid form. A great many of these phenomena occur at interfaces between electronic and electrolytic conductors where the passage of electric charge is connected with an electrochemical reaction, a so-called *Red-Ox reaction*:



where *Ox* is the oxidized species, *Red* is the reduced species, and *n* is the number of electrons exchanged between *Ox* and *Red*.

An electrochemical reaction is a heterogeneous chemical process involving the transfer of charge to or from an electrode, generally a metal, carbon or a semiconductor [28]. The charge transfer may be a cathodic process in which an otherwise stable species is reduced by the transfer of electrons from an electrode. Examples of such reactions which are important in electrochemical technology include:



Conversely, the charge transfer may be an anodic process where an otherwise stable species is oxidized by the removal of electrons to the electrode and relevant examples would be:



The number of reactant molecules involved in an electrode reaction is related stoichiometrically to the number of charges (electrons) flowing in the circuit. This is the basic argument of the laws formulated by Michael Faraday in 1832–1833 [29].

Faraday's law correlates the total charge, Q [C], passed through a cell to the amount of product, N [mol]:

$$Q = nFN, \quad (1.6)$$

where F is Faraday's constant, $F = 96485,3$ C/mol, and n is the number of electrons transferred per mole of product. Faraday's law can be used in many applications, such as electrogravimetry (to find the amount of substance deposited at an electrode) and coulometry (to find the total amount of electricity required for complete electrolysis of a compound); it can also be used for finding the number of electrons implicated in an electrolytic process. In order to reduce one mole of a generic reactant according to equation (1.1) ($n=1$), is needed to pass through the cell a total charge equal to 96500 C.

The rate of such a reaction can be followed with great sensitivity as an electric current. Such contacts constitute the electrodes of galvanic cells which can be used for the conversion of chemical into electrical energy in the form of batteries or for the generation of chemical products by electric power (electrolysis).

Conduction of electric current in conductors can be electronic or ionic, depending on the type of charge involved. Substances exist where conduction is mixed (i.e., where both ions and electrons are moving). *Electronic conduction* is found in all metals and also in certain other substances: carbon materials (graphite, carbon black), some oxides and other inorganic compounds (e.g., tungsten carbide), and a number of organic substances. *Ionic conductors* (conductors of the second kind) are also known as *electrolytes*. This term is used not only in the sense of an ionic conductor (e.g., in expressions such as "solid electrolytes," but also in a second sense, in speaking of substances that ordinarily are not conducting but produce ionic conduction after being dissolved in water or in another solvent (e.g., in terms such as "electrolyte solution" and "weak electrolyte") [29].

The main topic of electrochemistry is investigation of the properties of ionic conductors and of electric circuits containing ionic conductors, and investigation of phenomena occurring during passage of an electric current through such circuits.

The electrolyte contains at least two types of ions with opposite charge. In liquids, all ions are mobile and contribute to the conductivity. Their mobility is, however, different, and their individual contributions to the conductivity can therefore vary over wide ranges.

Cations move to the cathode, anions to the anode. If they are not consumed at the respective electrode at the same rate as they arrive there by ionic migration, they accumulate or deplete in front of this electrode, and the composition of the electrolyte changes in the region close to both electrodes in opposite directions. Such changes in composition can be used for the determination of transference numbers.

Conductivity is a very important parameter for any conductor [29]. It is intimately related to other physical properties of the conductor, such as thermal conductivity (in the case of metals) and viscosity (in the case of liquid solutions). The strength of the electric current I in conductors is measured in amperes, and depends on the conductor, on the electrostatic field strength E in the conductor, and on the conductor's cross section S perpendicular to the direction of current flow. As a convenient parameter that is independent of conductor dimensions, the current density i [A/cm^2] is used, which is the fraction of current associated with the unit area of the conductor's cross section:

$$i=I/S \quad (1.7)$$

The relationship between the concentration of oxidized species [Ox], concentration of reduced species [Red], and free energy (ΔG [J/mol]) (reaction 1.1) is given as

$$\Delta G = \Delta G^\circ + RT \ln \frac{[Red]}{[Ox]} \quad (1.8)$$

where R is the gas constant ($8.3145 \text{ J}/\text{mol} \cdot \text{K}$) and T [K] is the temperature. The critical aspect of this equation is that the ratio of reduced to oxidized species can be related to the Gibbs free energy change (ΔG), from which we can then derive the potential (E [V]):

$$\Delta G = -nFE \quad (1.9)$$

Here E is the maximum potential between two electrodes, also known as the open-circuit potential (OCP) or the equilibrium potential, which is present when no current is flowing through the cell, and F is Faraday's constant. If the reactant and product have unit activity, and E is for the reaction in the direction of reduction (left to right in equation (1.1)), then equation (1.9) can be written as

$$\Delta G^0 = -nFE^0 \quad (1.10)$$

In this case, the potential is known as the *standard electrode potential* (E^0 [V]) or the *standard potential* and it relates to the *standard Gibbs free energy change* (ΔG^0 [J/mol]). It should be noted here that due to the minus sign in equation (1.10), all spontaneous reactions (i.e., with $\Delta G^0 < 0$) will have a positive standard electrode potential ($E^0 > 0$).

The mathematical expression describing the correlation between potential and concentration for a cell reaction is a central tenant of electrochemistry and is known as the *Nernst equation* (obtained by combining equations (1.8)–(1.10)):

$$\Delta E = \Delta E^\circ + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad (1.11)$$

Each half-cell reaction has a specific standard potential reported as the potential of the reduction reaction vs. the normal hydrogen electrode (NHE). In an electrochemical cell, there is a half-cell corresponding to the working electrode (WE), where the reactions under study take place, and a reference half-cell. Experimentally the cell potential is measured as the difference between the potentials of the WE half-cell and the reference electrode/reference half-cell. The archetypal reference electrode is the NHE, also known as the standard hydrogen electrode (SHE) and is defined, by convention, as 0.000 V for any temperature.

1.2. Cathodic metal deposition

Many metals are made by electrodeposition. Several metals are prepared by electrolysis in molten salts. A variety of plating processes have been developed for the metals deposited by electroplating. Cathodic deposition (electrocrystallization) of metals is the basic process in electrometallurgy and electroplating.

Electrodeposition is an extremely important technology. Covering inexpensive and widely available base materials with plated layers of different metals with superior properties extends their use to applications which otherwise would have been prohibitively expensive [30]. However, it should be noted that electroplating is not a simple dip and dunk process. It is probably one of the most complex unit operations known because of the unusually large number of critical elementary phenomena or process steps which control the overall process [31].

Two types of metal deposition are distinguished: that on the same metal and that on a substrate (matrix) consisting of another metal. In the latter case a number of special features can arise.

1.2.1. Underpotential deposition of metal atoms

Because of the energy of interaction between a foreign substrate and the adsorbed metal atoms formed by discharge, cathodic discharge of a limited amount of metal ions producing adatoms is possible at potentials more positive than the equilibrium potential of the particular system, and also more positive than the potential of steady metal deposition.

1.2.2. Incorporation of metal

In certain cases, metal atoms, after their discharge, can penetrate into the substrate metal, forming alloys or intermetallic compounds in the surface layer and down to a certain depth. This effect has been known for a long time in the discharge of metals at liquid mercury, where liquid or solid amalgams are formed. In 1968 B. Kabanov showed that an analogous effect is present in metal ion discharge at many solid metals.

1.2.3. Epitaxy

In many cases, the structure of the deposit will duplicate that of the substrate when the crystallographic parameters of the metal being deposited are not overly different from those of the substrate metal (not by more than 15%). The influence of substrate structure can extend to several thousand atomic layers of the metal being deposited (which is equivalent to a deposit thickness of up to 1 μm). Epitaxy is pronounced in deposits of copper, silver, and zinc.

An important problem in metal deposition is the quality of adhesion of the deposit to the substrate (both foreign and native). In electroplating, one of the major requirements is high strength and reliability of adhesion. In electrohydrometallurgy and electroforming, metals are often deposited on a foreign matrix, and then separated from it; here, to the contrary, poor adhesion is required. The quality of adhesion — apart from other possible factors — depends on the structure and cleanliness of the substrate surface. Hence, prior to the start of deposition the substrate is carefully conditioned both by mechanical (grinding, polishing) and chemical (etching, degreasing) means.

After formation of a primary deposit layer on foreign substrates, further layer growth will follow the laws of metal deposition on the metal itself. But when the current is interrupted even briefly, the surface of the metal already deposited will become passivated, and when the current is turned back on, difficulties will again arise in the formation of first nuclei, exactly as at the start of deposition on a foreign substrate. This passivation is caused by the adsorption of organic additives or contaminants from the solution. Careful prepurification of the solution can prolong the delay with which this passivation will develop.

1.2.4. Polarization in metal deposition

In the steady state, polarization in the case of poorly polarizable metals arises primarily from limitations in the rate of reactant supply (concentration polarization) and from phenomena associated with crystallite growth. In the case of highly polarizable metals, an

appreciable activation polarization that is associated with the step of metal ion discharge is found, and the contribution due to growth of the new phase is slight against this background. Experience shows that for such metals the values of polarization in electrocrystallization are similar to those in metal ion discharge at the mercury electrode (where a new phase is not formed). Polarization in metal deposition is highly sensitive to solution composition. When present in the solution, a number of complexing agents and surfactants will strongly enhance it. In electroplating, it is very common that metals are deposited from solutions of their complex salts.

1.2.5. Parallel reactions

For many metal–solution systems, the equilibrium electrode potential is more negative than the equilibrium potential of the reversible hydrogen electrode in the same solution. However, even if it is not, polarization during cathodic metal deposition may push the electrode potential to a value more negative than that of the NHE. Then cathodic hydrogen evolution will occur in parallel with metal ion discharge (as long as the polarization of hydrogen evolution at the metal is not very high).

Parallel hydrogen evolution can have two effects.

1. In contrast to metal ion discharge, hydrogen evolution according to reaction (1.2) causes a pH increase of the solution layer next to the cathode. At a certain value of pH in this layer, hydroxides or basic salts of the metal start to precipitate, which affects the mechanism of further metal deposition and also the structure and properties of the deposit produced.

2. In simultaneous hydrogen ion discharge, the resulting adsorbed hydrogen atoms are incorporated into the growing metal deposit. This alters the mechanical properties of the metal; hydrogen embrittlement occurs. This effect is pronounced in the iron group metals, but is less distinct in copper and zinc. It is not observed in cadmium or lead deposition.

When ions of different metals, M_1^{n+} and M_2^{n+} , are present together in the solution, simultaneous discharge of the ions and alloy formation between the two metals is possible. To this end the electrode potential must be more negative than that of the more electronegative metal. When the concentration of ions of the more electropositive metal is low, the electrode potential will shift to the said value as a result of concentration polarization. However, when the concentration of these ions is high, the equilibrium potentials of the two metals are highly different, and metal M_2 is poorly polarizable, discharge of the more electronegative ions will be hindered. In this case the equilibrium potentials of the two metals can be moved closer

together by suitably selected complexing agents. The electrolytic formation of metallic alloys is practiced in a number of technical fields.

The refining (purification) of metals rests on the separate dissolution and cathodic redeposition of different metals. In the anodic dissolution of the original metal sample, other more electronegative metals present as impurities dissolve together with the base metal. More electropositive impurity metals will not dissolve, but sediment as a sludge that can then be separated from the solution. During the ensuing cathodic deposition of base metal from the solution obtained, the electronegative impurity metals will not deposit at the potential selected but remain in solution. In this way a rather complete separation of the base metal from other metals, both more electropositive and more electronegative, is attained. Highly pure metals can be obtained by prior fractional metal deposition at mercury and subsequent fractional redissolution from of the resulting amalgam.

The principle components of an electroplating process are shown schematically in Fig. 1.1.

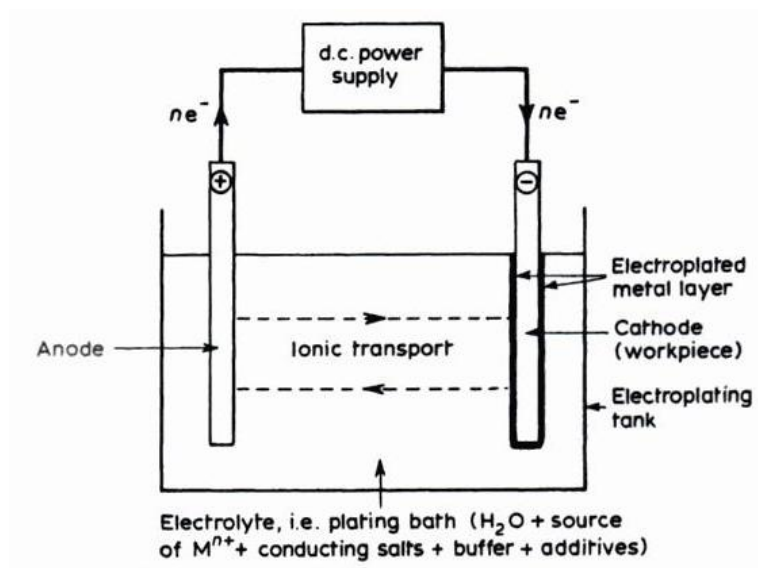


Figure 1.1: *Principle of electroplating*

1. An electroplating bath containing a conducting salt and the metal to be plated in a soluble form, as well as perhaps a buffer and additives.
2. The electronically conducting cathode, i.e. the workpiece to be plated.
3. The anode (also electronically conducting) which may be soluble or insoluble.
4. An inert vessel to contain (1-3), typically, e.g. steel, rubber-lined steel, polypropylene or polyvinylchloride.
5. A d.c. electrical power source, usually a regulated transformer/rectifier.

2. Literature review of niobium electrodeposition

2.1. Introduction

All electrochemical reactions and phenomena occur in a medium, usually a solvent containing dissolved ions (often called the supporting electrolyte or just the electrolyte) which are mobile and able to support current flow. The properties of this medium (which we will call the solvent–electrolyte combination, or sometimes the electrolyte for short) are critically important to any electrochemical experiment. A medium containing mobile ions must exist between the electrodes in an electrochemical cell to allow for control and/or measurement of the electrode potential in the cell, which is required in nearly all electrochemical experiments. A medium with good solvating power is needed to dissolve reactants and products from the electrode reaction, and one with reasonably low viscosity is often needed to allow for rapid transport of reactants and products to and from electrodes. Finally, a medium with low reactivity, or at least with a specific desired reactivity, is needed that will be compatible with oxidizing and reducing electrodes and with reactive species which might be created at electrodes, for any of a wide variety of reasons including analysis, synthesis, energy conversion, or simply the novelty of making a new species for the first time and studying its properties [30].

2.2. Aqueous electrolyte solutions

Aqueous solutions of acids, bases, and salts are the ionic conductors used most widely and studied most thoroughly. The importance of other types of ionic conductors has increased in recent times, but aqueous solutions are still preeminent. Their significance goes far beyond electrochemistry as such; they can be found in practically all spheres of human activity. They are of exceptional importance in the form of intracellular fluids in the biological and physiological processes of all living beings. They are of equally great importance in the form of natural waters in the oceans, rivers, and underground for geomorphological processes.

Aqueous electrolyte solutions have been a subject of determined studies for over a century. Numerous attempts were made to construct theories that could link the general properties of solutions to their internal structure and predict properties as yet unknown. Modern theories of electrolyte solutions are most intimately related to many branches of

physics and chemistry. The electrochemistry of electrolyte solutions is a large branch of electrochemistry sometimes regarded as an independent science [29].

Notwithstanding to the fact that the electrodeposition of niobium thermodynamically is not possible from aqueous solutions because the potential for this metal falls outside the window of stability for water (Figure 0.1), there is some information in literature about aqueous-based electrolytes which were proposed for niobium electroplating.

There are no simple, stable to hydrolysis salts of niobium which could be used for preparing of stable aqueous electrolytes. Using chemically synthesized complexes of niobium for preparation of electrolytes is limited. Aqueous solutions of niobium pentoxide or fluoroniobates are very easy exposed to hydrolysis.

Electrolytes were prepared by electrochemical dissolution of niobium with a.c. current in fluoboric acid (50-150 g/l) with addition of complexing agent OK-3 and stabilizing agent PV-20 [29].

For electrodeposition Ni-Nb and Fe-Nb alloys in initial niobium-contained electrolyte were added nickel or iron-contained salts and EDTA with next neutralization by ammonium hydroxide. Composition of components in electrolytes is shown in Table 2.1

The maximum content of niobium in alloys was observed with co-deposited components ratio in electrolyte – Nb:Ni (Fe) = 2:1. There are 6% of niobium in Ni-Nb alloy and 10% - in Fe-Nb alloy. With decreasing of niobium concentration in electrolytes (Nb:Ni (Fe) = 1:1, Nb:Ni (Fe) = 1:2) was observed appreciable decreasing of niobium content in alloys.

Component, g/l	Ni-Nb alloy	Fe-Nb alloy
Nb	10-20	10-20
NiCO ₃	10-20	-
FeCl ₂	-	10-20
HBF ₄	50-150	50-150
EDTA	30-40	30-40
OK-3	100-150	100-150
PV-20	10-30	10-30
NH ₄ OH (25%- water solution)	For pH 2,5 – 3	For pH 1,5 – 2

Table 2.1: *Aqueous electrolytes for electrodeposition of Ni-Nb and Fe-Nb alloys*

Composition of electrolytic alloys Ni-Nb and Fe-Nb also depends of cathodic current density. With increasing of current density the content of niobium in alloys increases. With increasing of solution pH from 2 to 3 the content of niobium in alloys decreases.

The quality of Ni-Nb coating depends of temperature. The best properties of Ni-Nb alloys with mirror-like brightness were obtained with temperature 50-70°C (current density 5-

20 A/cm²). The properties of Fe-Nb alloys not depend of temperature and coatings were deposited with room-temperature. Current density was 5-15 A/cm² [32].

For electrodeposition of niobium is known aqueous electrolyte (Table 2.2) on the base of niobatic acid, with current efficiency of niobium – 0,1% [33]

Component	Concentration, g/l
HNbO ₃	15-17
HF	120-140
NH ₄ F	15-20
Formaldehyde	7-15

Table 2.2: *Electrolyte for electrodeposition of niobium*

Temperature of electrolysis is 40-60°C, current density – 10-20 A/dm². Must be done pre-electrolysis of electrolyte during 2 hours. With increasing of temperature and current density coatings changes their color from shining light-grey to shining dark-grey.

Another electrolyte which suggested for niobium electroplating is based on fluoboric acid (10-550 g/l) and hydrochloric acid (50-300 g/l) with additions of fluorides (10-30 g/l) [34]. Niobium in these electrolytes is placed by method of electrochemical synthesis – direct dissolution of metal under alternating current of high amplitude. Dissolution was done with current density 2,5 – 14 A/dm². After preparation solutions were stabilized with complexing agents OK-3 and PV-20.

Very low current efficiency of aqueous electrolytes and high instability because of hydrolysis of niobium compounds make the process of niobium electrodeposition from these electrolytes very difficult.

In order to exclude side reaction of hydrogen reduction and hydrolysis of components non-aqueous electrolytes for niobium deposition were suggested. There are: electrolytes with organic solvents, high-temperature melts and ionic liquids.

Some of the advantages of using non-aqueous solutions for metal deposition are the possibility of depositing metals that can't be discharged from aqueous solutions, the deposition of metals at higher cathode efficiencies, the possibility of obtaining greater coating thicknesses where these are known to be limited in the corresponding aqueous systems and the deposition of commoner metals onto reactive substrates such us titanium and uranium [35].

2.3. Electrolyte with organic solvents

Many organic liquids (in addition to water) have been used as solvents for electrochemical experiments. One important property of organic solvents is the ability to dissolve and dissociate salts to achieve a reasonably high ionic conductivity. The other general solvent property category that is often especially important in electrochemistry is reactivity, including acidity/basicity, nucleophilicity/electrophilicity, redox, polarity, and many other types of reactivities which are limited only by the chemistry one is attempting to perform on the solvent. Susceptibility to oxidation or reduction is especially important in electrochemistry since the solvent is often in contact with electrodes that are held at very oxidizing and/or reducing potentials, and at which highly oxidized and/or reduced species are produced. Figure 3.1 presents a summary of selected potential limits for some common combinations of solvent, electrolytes, and electrode. Other factors that can be important include liquid range, optical properties, volatility, toxicity and cost.

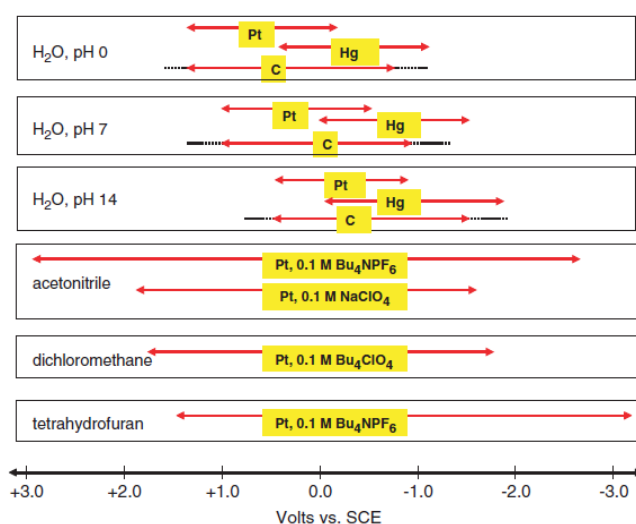


Figure 2.1: *Potential limits for some selected combinations of solvent, electrolyte, and working electrode* [30]

The compact shining coatings of Ni-Nb alloy with thickness not more than 1 μm and niobium content in alloy less than 1% could be obtained from electrolyte with next composition (Table 2.3) [36].

Component	Concentration, g/l
NbCl ₅	40-100
NiCl ₃	0,1 – 0,3
Ethanol	96-100%

Table 2.3: *Electolyte with organic solvent for electrodeposition of Ni-Nb alloy*

Current efficiency of this electrolyte is 0,5-1%. Coatings were obtained with current density $0,2 \text{ A/cm}^2$. Also as organic solvent could be used propanol or butanol.

There is information about electrodeposition of niobium in pure metallic form from complex organic electrolyte (Table 2.4.) [37].

Component	Concentration, g/l
NbCl ₅	10-15
Methanol	300-500 ml/l
Benzol	500-600 ml/l
Propyl acetate	20-30 ml/l

Table 2.4: *Electolyte with organic solvents for electrodeposition of niobium*

Cathodic current density is $5-15 \text{ mA/cm}^2$, duration of electrolysis is 10 minutes. The thickness of film is $1 \mu\text{m}$. The cathodic material was stainless steel, the anodic – niobium.

The extreme high vapor pressure, flammability and explosiveness make these solutions very dangerous.

2.4. High-temperature melts

Separation of the ions in an ionic crystal is possible not just with dissolving but also by thermal energy. At higher temperatures the crystals melt which gives the ions a certain amount of free mobility. While pure salts have relatively high melting temperatures, mixtures of different salts form eutectic systems with considerably lower melting points [38].

Molten salts represent a unique class of electrochemical systems. These materials may be corrosive, moisture- or oxygen-sensitive, and/or with a high melting temperature. All these factors must be taken into account in the design of electrochemical cells for molten salt research.

The difficulties associated with H₂ co-reduction are mostly avoided by the use of molten salt media. Further, two of the counter difficulties offered by the use of organic solvent systems (low conductivity and low limit of current) are greatly diminished, at least in high-temperature systems ($250 < T < 1000^\circ\text{C}$). As to the downside of molten salt systems, it is

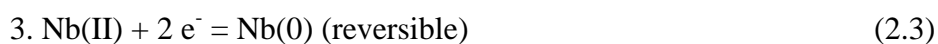
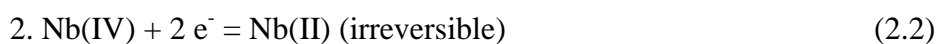
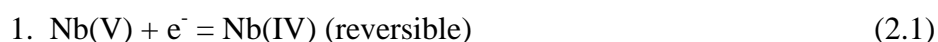
the increased expense of sustaining them in a stable state, mainly ensuring a limited corrosion rate of the containing vessel, and the reduction of contamination of the system with any breakdown products from such corrosion. Residual water - which might well have been thought to have been boiled off at $>100^{\circ}\text{C}$ – sometimes is retained for many hours in the salt, but is a lesser threat than it is in anhydrous organic systems. The window of operation can be as high as in the non-aqueous systems and is seldom less than 4 V (1,5 - 1,6 V in aqueous systems) [39].

The ionic conductivities of most solid crystalline salts and oxides are extremely low. The ions are rigidly held in the crystal lattices of these compounds and cannot move under the effect of applied electric fields. When melting, the ionic crystals break down, forming free ions; the conductivities rise drastically and discontinuously, in some cases up to values of over 100 S/m (i.e., values higher than those of the most highly conducting electrolyte solutions) [29].

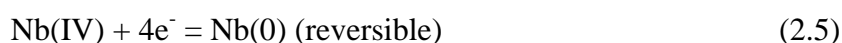
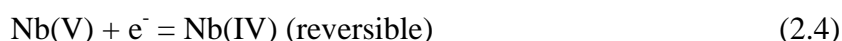
B. Gillesberg et al. obtained niobium from alkali chloride melts on nickel and AISI316 stainless steel substrates both by constant current and by pulse current methods. No metallic niobium was obtained at temperatures below 500°C . At temperatures between 550 and 650°C , the deposits were dendritic and non-adherent, whereas pure niobium layers could be obtained at 750°C [40].

The electrodeposition of niobium from a binary electrolyte consisting of KF and NaF was characterized and compared with that from the ternary electrolyte of LiF, NaF and KF (FLiNaK) by Capsimalis, Chen and Peterson [41]. The deposition experiments were conducted at current densities between 5 and 35 mA/cm^2 and electrolyte temperatures between 725 and 800°C . It was necessary to operate both electrolytes above 725°C to obtain dense coherent deposits. The procedure for preparing the fused niobium electrolytes involved the addition of 3,2 wt % K_2NbF_7 to the binary eutectic and 2,5wt% to the ternary eutectic, and outgassing the mixture under vacuum at 400°C for one week to remove adsorbed moisture.

The temperature effect on the mechanism of electroreduction niobium complexes has been observed in the LiCl-KCl-NbCl₅ melt [42]. At a temperature below 903-923K, the electroreduction of niobium proceeds in a three-step mechanism:



It should be added that the second step of electroreduction is complicated by the formation of insoluble cluster compounds owing to the reaction of Nb(IV) and Nb(II) complexes. At the second step, NbCl_{2,33} cluster compound and a large assortment of nonstoichiometric compounds in the composition range NbCl_{2,67} - NbCl_{3,13} have been obtained by potentiostatic electrolysis. The electrolysis at more negative potentials leads to an increased amount of niobium in the cathodic deposit. At the third step, the Nb(II) complexes still not reacted with Nb(IV), or reduced from cluster compounds, are discharged to the metal. At temperatures above 923K, the second and third waves merge into a single four-electron wave, and the formation of cluster compounds of the NbCl_x type becomes thermodynamically unfeasible. The voltammograms display only two reduction waves:



At a temperature higher than 923K, the deposition of niobium is not complicated by the formation of sub-chloride impurities.

The number of steps and the mechanism involved in the electroreduction of complexes is affected most strongly, by the anionic composition of the melt, as it determines the composition of the first coordination sphere. The relevant data on the effect of the anionic composition of the melt on the mechanism involved in the electroreduction of niobium complexes in a NaCl-KCl melt are listed in Table 2.5.

Element	Mechanism of electroreduction in melts		
	chloride	chloride-fluoride	oxofluoride
Niobium [43; 44; 45; 46]	I Nb(V) + e ⁻ = Nb(IV) (R) II Nb(IV) + 4 e ⁻ = Nb (R)	I Nb(V) + e ⁻ Nb(IV) (R) II Nb(IV) + 4 e ⁻ = Nb (IR)	I Nb(V) + 5e ⁻ = Nb (Q); at v ≤ 2.0 V/s complicated by preceding chemical reaction

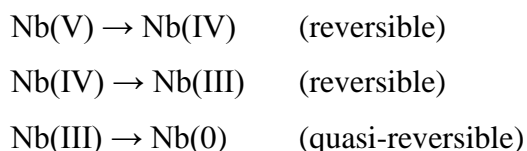
Note: (R), reversible process; (IR), irreversible process controlled by charge transfer rate; (Q) quasi-reversible process.

Table 2.5: *Mechanism of niobium electroreduction in molten salts.*

The influence exerted by the anionic composition of the melt depends on the element, but a common feature is that an increase in the basicity of the melt reduces the number of discharge steps and causes the discharge of complexes to the metal to change from a reversible to an irreversible process.

For niobium, four oxidation states are detected during the reduction of NbCl_5 dissolved in LiCl-KCl : Nb^{5+} , Nb^{4+} , Nb^{3+} and Nb^{2+} ; moreover, complexed compounds, such as Nb_3Cl_8 , appeared at the electrode surface. These intermediate compounds, often sparingly soluble, remain adsorbed at the electrode surface and disturb the metal deposition [47].

In LiCl-KCl at 450°C Nb(V) , Nb(IV) and Nb(III) species are stable [48]. It was found that the reduction of solutions of NbCl_5 occurred via a multistep mechanism [47]:



This last step is perturbed by the formation of insoluble sub-halide compounds. To avoid this inconvenience, the electrolysis was performed at a higher temperature in the NaCl-KCl mixture [49].

It has been shown that introducing fluoride ions has a beneficial effect on the quality of the niobium deposit and stabilizes the higher oxidation states [50].

Different niobium alloys with specific properties were obtained from high-temperature melts.

Electrodeposition of niobium coatings on graphite with subsequent precise surface alloying of niobium with hafnium was studied by Kuznetsov and Kuznetsova [51]. Electrochemical synthesis of Nb-Hf coatings from molten salt systems containing compounds of niobium and hafnium was used too. It was shown that Nb-Hf coatings with a planar growing front can be obtained if the concentration and therefore the limiting current density of the more electropositive component Nb is kept low. Nb-Hf coatings with a thickness of 20-30 μm have been obtained in this way from an $\text{NaCl-KCl-K}_2\text{NbF}_7(1 \text{ wt\%})\text{-K}_2\text{HfF}_6(10 \text{ wt\%})\text{-NaF}(5 \text{ wt\%})$ melt, above the limiting current density of niobium deposition.

Polyakova, Taxil, Polyakov reported that for electrodeposition of niobium-titanium alloys can be used NaCl-KCl-NaF -melts with K_2TiF_6 and K_2NbF_7 [52]. The choice of the electrolyte was due to the fact that preliminary investigations showed instability of the highest valency of titanium and niobium in NaCl-KCl melt. The addition of sodium fluoride prevented the spontaneous transition of $\text{Nb(V)} \rightarrow \text{Nb(IV)}$ and $\text{Ti(IV)} \rightarrow \text{Ti(III)}$, made the melts stable and provided reproducible data.

Nickel-niobium alloys have been shown to have the properties required of insoluble anodes [53] as well as excellent electrocatalytic activity [54]. Fang Baizeng and Liu Xinyu are trided to obtain nickel-niobium alloy films on a nickel surface by an electrochemical process

in molten fluoride and to try to apply niobium-modified nickel film on molten carbonate fuel cell (MCFC) anodes [55].

The preparation of the nickel-niobium surface alloy was carried out by electrochemical reduction of niobium(IV) ions on a nickel cathode in molten fluorides. Niobium foils were used as the anode and reference electrode. A eutectic mixture of 50mol% NaF + 50mol% LiF was used as a solvent for electrochemical alloying of nickel with niobium at 750°C. Melt purification was performed as follows: the bath was initially dehydrated by heating under a vacuum (1 Pa) for 24 h at 500°C, then melted under an argon atmosphere at 750°C. Niobium (IV) ions were generated in situ by addition of potassium heptafluoroniobate(V) and metallic niobium to the bath. The following reaction occurs:



Polarization experiments reveal that the corrosion resistance as well as the electrocatalytic activity of the niobium-modified electrode (nickel-niobium surface alloy) is superior to that of an unmodified one. Surface modification of a MCFC anode can be employed to improve the polarization performance of the electrode material.

One of the major drawbacks of any molten salt process for electrodeposition is the energy needed to maintain the system in its molten state. The energy that is added either by external heaters or by Joule heating must add to the cost of the final product.

2.5. Low-temperature melts

AlCl₃-NaCl melts exhibit some attractive properties such as low melting temperatures and good solubilities for various compounds.

AlCl₃ make with NaCl deep eutectic with temperature close to 190°C which much less than melting point of these pure salts. This eutectic wildly used for aluminum electrodeposition. Also there is information about electrodeposition of aluminium alloys from molten chloroaluminates.

Aluminium alloys with with small contents of refractory metals have excellent resistance against pitting corrosion [56]. It has been demonstrated that Al-Nb alloys can be deposited from chloroaluminate melts containing dissolved niobium species [57].

Electrodeposition of aluminium alloys with niobium, molybdenum and tantalum from molten NaCl-AlCl₃ (48-52 mol%) at 190°C was studied by Geir Martin Haarberg and Gery Stafford [58]. Dissolved niobium, molybdenum and tantalum species were formed by anodic dissolution of the pure metals. It was confirmed that aluminium alloys containing Nb, Mo or

Ta could be electrodeposited. However, none of these metals could be deposited in the pure form.

The electrochemistry of Nb(V) was reinvestigated in oxide-free $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ and in fluorochloroaluminates [59]. Nb(V), added to an oxide-free NaCl saturated NaAlCl_4 melt at 178°C as NbCl_5 , was present in the melt as such together with some NbCl_6^- as demonstrated by the UV-visible spectra. The spectral changed induced by the addition of oxide to the melt clearly demonstrated formation of a moiety niobium oxychlorides. The same type of evidence was obtained by cyclic voltammetry in the presence of absence of oxide.

Sato [60] has reported that Nb_3Cl_8 added to 55 m/o $\text{AlCl}_3\text{-NaCl}$ can lead to Nb-Al alloys containing up to 18 a/o Nb. The limitation appears to be the low solubility of Nb_3Cl_8 in the electrolyte. When the electroactive niobium species was formed by the anodic dissolution of metallic niobium, significantly higher alloy compositions, up to 35 a/o Nb, were reported.

Attempts were made to produce Nb_3Al from an acidic NaCl-AlCl_3 melt at 473 K. Nb-Al alloys up to 75–80 wt.% niobium content were obtained. This composition corresponds to an equimolar composition of niobium and aluminum rather than the desired composition (91.2 wt.% Nb).

Pure metallic niobium wasn't obtained from molten chloraluminates, just in alloy with aluminium. That's why a new class of molten salts with low melting points ($<100^\circ\text{C}$) has come into focus for research, which is room temperature ionic melts or ionic liquids.

2.6. Ionic liquids

Ionic liquids are compounds comprising organic cations and inorganic or organic anions. that have melting points below 100°C [61]. Because the choice of the anionic and cationic components affects the properties of the ionic liquids, they can be regarded as designer solvents [62]. Ionic liquids possess some remarkable properties [38]:

- They are liquid at temperatures between room temperature and 100°C .
- They are inflammable and have high thermal stability.
- Newly developed ionic liquids also have hydrophobic properties that allow handling in air.
- They have a negligible vapor pressure.

- Their large electrochemical potential window (Figure 2.2 and 2.3) allows electrochemical processes that are not possible in aqueous electrolytes such as deposition of metals that are not deposable in aqueous electrolytes.

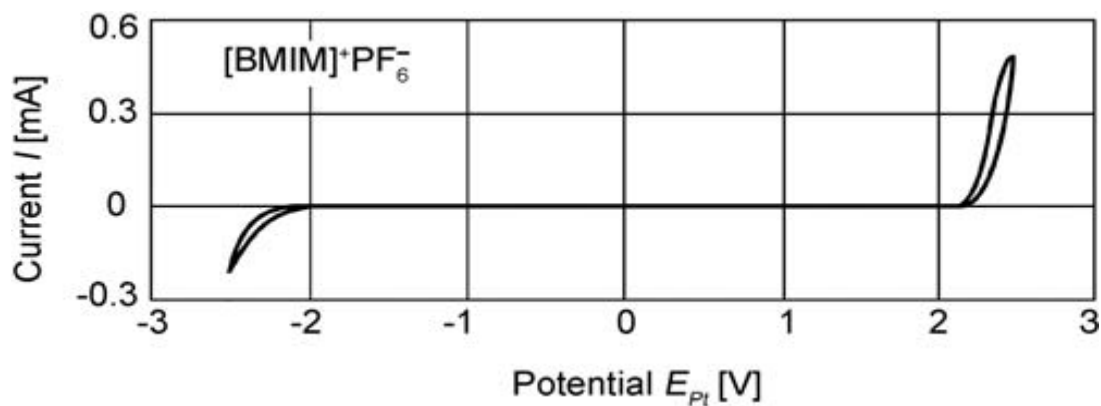


Figure 2.2: Electrochemical potential window of neutral 1-butyl-3-methyl imidazolium hexafluorophosphate ($[BMIM]^+PF_6^-$)

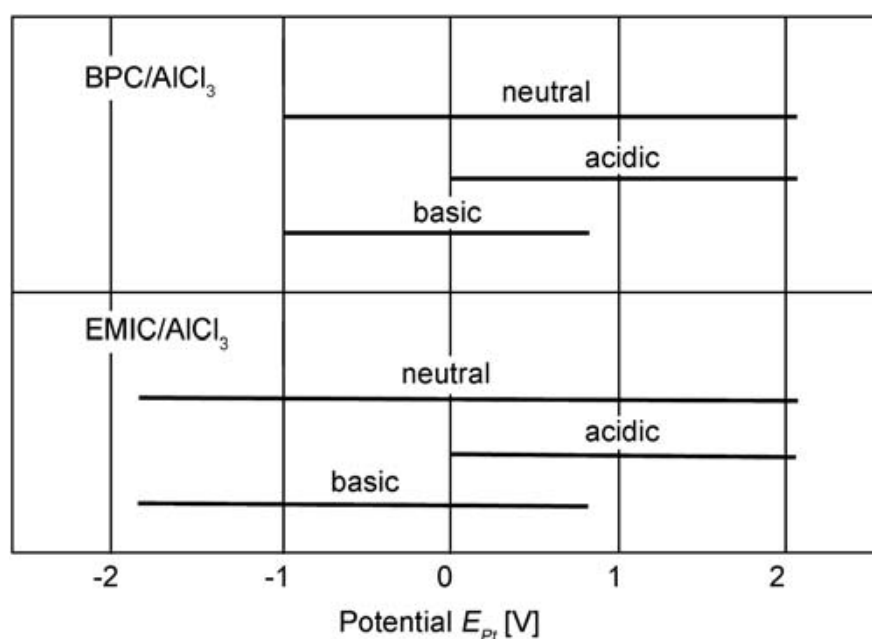


Figure 2.3: Electrochemical potential windows of *N*-butyl-pyridinium chloride (BPC) and 1-ethyl-3-methyl imidazolium chloride (EMIC) in the presence of $AlCl_3$

Originating from electrochemistry in $AlCl_3$ based liquids an enormous progress was made during the recent 10 years to synthesize ionic liquids that can be handled under ambient conditions, and today about 300 ionic liquids are already commercially available.

The first discovered room-temperature ionic liquid seems to be ethylammonium nitrate, [EtNH₃][NO₃] [63], described at the beginning of XX century (1914). In the middle of the last century (1948) the first room-temperature ionic liquid based on chloroaluminate anion was patented [64; 65]. Fifteen years later (1963), a similar system, based on chlorocuprate anion, CuCl₂⁻ and tetraalkylammonium cation, obtained by mixing cuprous chloride (CuCl) and tetraalkylammonium chloride, was described [66]. In 1967 the application of tetra-*n*hexylammonium benzoate as a solvent was published [67]. The class of ionic liquids, based on tetraalkylammonium cation and chloroaluminate anion, has been extensively studied since late 1970s of the XX century, following the works of Osteryoung [68]. Systematic research on the application of chloroaluminate ionic liquids as solvents was performed in 1980s [69]. The most extensively studied room-temperature ionic liquid of this type seems to be dialkylimidazolium chloroaluminates. Such room-temperature ionic liquids are good solvents for conducting various reactions as AlCl₃ is an acid in the Lewis meaning and can act as a catalyst. However, ionic liquids based on aluminium halides are moisture sensitive, as AlX₃ reacts with water with the liberation of HX (X =Cl⁻ or Br⁻). In the 1990s new ionic liquids were described, based on 1-ethyl-3-methylimidazolium cation and tetrafluoroborate anion, resistant to moisture traces [70] and showing clearly that the room temperature ionic liquids are not limited to uncomfortable chloroaluminate salts. During the last decade an increasing number of new ionic liquids have been prepared and used as solvents.

2.6.1. Classification of ionic liquids according to acidity/basicity

The design and choice of ionic liquids commonly focuses on physical properties such as water-miscibility, conductivity, viscosity and solubility properties, although how the chemical structure of the ionic liquid affects these various characteristics is still poorly understood. However, there is another chemical property that imparts a variety of physical characteristics to the ionic liquids that has been little investigated; the relative acidity or basicity of the component ions.

2.6.1.1. Neutral anions

Typical ionic liquid anions are those that can be described as neutral in the acid/base sense or very weakly basic; these exhibit only weak electrostatic interactions with the cation and thus impart advantageously low melting points and viscosities. Included in this class are anions such as hexafluorophosphate, *bis*(trifluoromethanesulfonyl)amide (TFSA, also known as TFSI and $(\text{Tf})_2\text{N}$), tetrafluoroborate, methanesulfonate (mesylate), thiocyanate, tricyanomethide and *p*-toluenesulfonate (tosylate) (Figure 2.4). Ionic liquids formed from

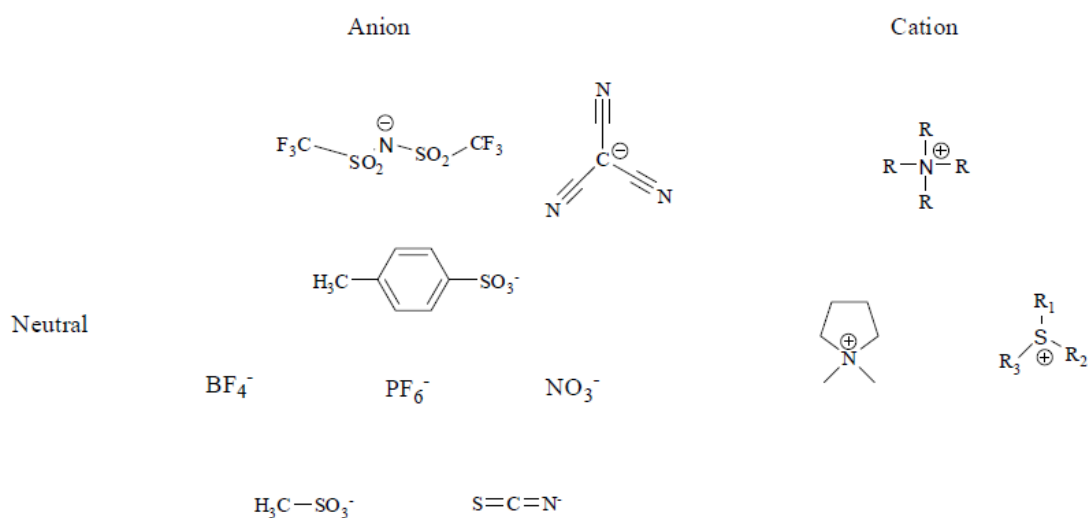


Figure 2.4: Scheme of neutral anions and cations

these anions typically exhibit good thermal and electrochemical stability and thus are often utilized as inert solvents in a wide range of applications [71].

2.6.1.2. Acidic cations and anions

The simplest examples of slightly acidic ionic liquids are those based on the protic ammonium, pyrrolidinium and imidazolium ions, of which many are known. The well known AlCl_3 based ionic liquids are Lewis acidic when they contain an excess of AlCl_3 (Figure 2.5) [72].

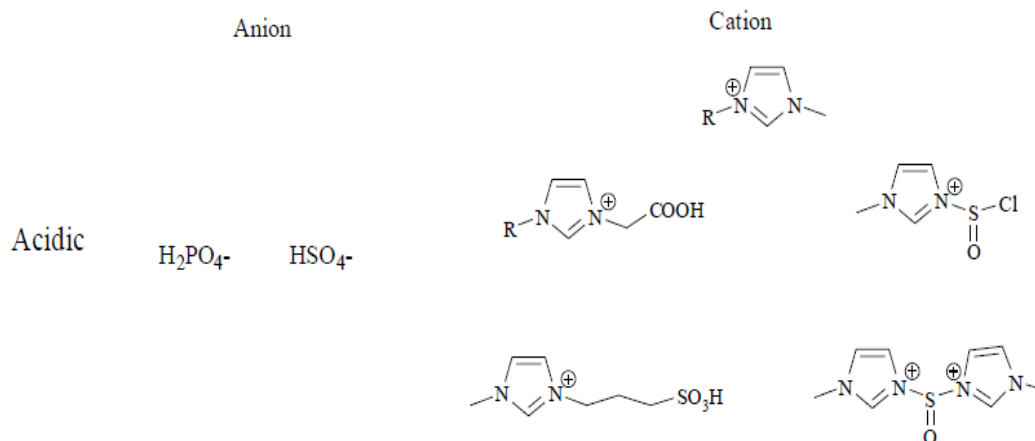


Figure 2.5: Scheme of acidic anions and cations

2.6.1.3. Basic cations and anions

There are a number of ionic liquid forming anions that can class as basic. These include the lactate, formate, acetate (and carboxylates generally) and the dicyanamide (dca) anion. The dicyanamides, in particular, have become readily available because of their low viscosity, including as phosphonium salts. Since the basicity of these anions imparts different, advantageous properties to the ionic liquids, such as different solubilizing and catalytic properties, as discussed below, this category of ionic liquids is likely to grow considerably in the coming years.

An alternative to the design of ionic liquids utilizing a basic anion is to incorporate a basic site into the cation. This may afford more thermally stable ionic liquids than those containing basic anions, which frequently exhibit relatively low decomposition temperatures (Figure 2.6) [73].

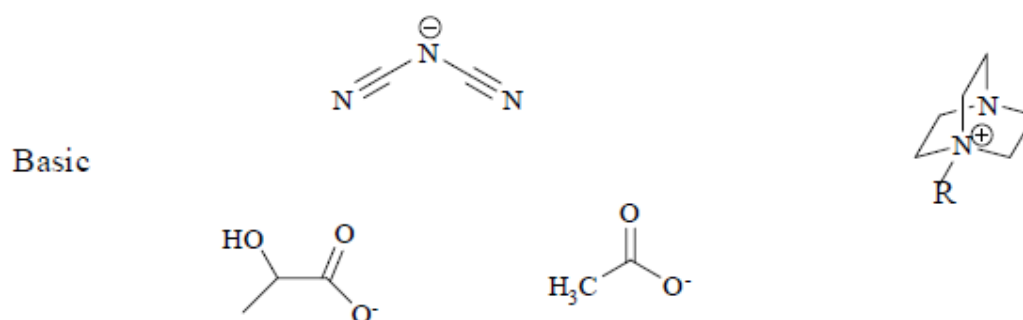


Figure 2.6: Scheme of basic anions and cations

2.6.1.4. Amphoteric Anions

There are a small number of ionic liquid anions that fall into the interesting class of amphoteric anions, with the potential to both accept and donate protons depending on the

other substances present. The hydrogen sulfate (HSO_4) and dihydrogen phosphate (H_2PO_4) anions are simple examples of such anions [73].

2.6.2. Conductivity

Generally, conductivity of the order of 10 mS/cm is typical of ionic liquids based on $[\text{EMI}]^+$. On the other hand, ionic liquids based on tetraalkylammonium, pyrrolidinium, piperidinium and pyridinium cations are characterised by considerably lower conductivities, in the range between 0,1 and 5 mS/cm. Even the highest room temperature ionic liquid conductivity is much lower in comparison to conventional aqueous electrolyte solutions applied in electrochemistry. For example, the specific conductivity of aqueous KOH (29,4 wt.%) solution, applied in alkaline batteries, is 540 mS/cm. The electrolyte applied in lead-acid batteries, 30 wt.% aqueous H_2SO_4 , shows a conductivity at the level of ca. 730 mS/cm. However, nonaqueous solutions show one order of magnitude lower conductivity [74].

2.6.3. Electrochemical stability

Electrolytes for application in electrochemical devices should be resistant for electrochemical reduction and oxidation.

The stability windows are reported to be in a broad range from 2 to 6V. Halide anions such as F^- or Br^- , which undergo anodic oxidation at relatively low potentials, are responsible for a narrow stability of the order of ca. 2-3V. The amide anion, $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$, on the contrary, is oxidised at relatively high anodic potentials, which implies the broad stability of ionic liquids based on this anion. The most common stability is around 4,5V. On the other hand, ionic liquids based on tetraalkylammonium cations, which show cathodic reduction at relatively negative potentials, are characterised by enhanced stability (4,0–5,7 V). Stability windows obtained at Pt and glassy carbon electrodes are comparable. On the other hand, the ionic liquids/tungsten interface shows much enhanced stability of the order of ca. 6,5–7V. Both the reduction potential of cation and that of anion oxidation depend on the counter-ion [74].

2.6.4. Electrodeposition of Nb and Nb alloys using ionic liquids

The most widely used ionic liquid for electrodeposition metals which are hard obtained from aqueous solution is aluminum chloride : 1-ethyl-3-methylimidazolium chloride (EMIC) room-temperature molten salt.

Cheek and Trulove have studied the electrochemical properties of niobium in the aluminum chloride : 1-ethyl-3-methylimidazolium chloride (EMIC) room-temperature molten salt system in order to understand the processes occurring during electrodeposition of this metal from the acidic (molar excess of AlCl_3) melt [75]. Such conditions allow the co-deposition of this metal with aluminum, conferring anti-corrosion properties on the resulting films.

Electrochemical reduction of NbCl_5 in an acidic melt shows a well-defined one-electron cyclic voltammetric process, followed by further reduction in a more complicated process, predominantly to the trivalent state [76]. It is possible that niobium cluster compounds are formed at this point. Further reduction to the metallic state evidently does not occur, because a stripping peak for niobium oxidation is not observed even with a negative-going scan ending just before aluminum deposition.

Electrodeposition of Nb evidently occurs with aluminum deposition; however, the product obtained is a powder rather than an adherent film. Attempts to produce niobium deposits at lower concentrations (low mM), and therefore lower current densities, were only partially successful, probably due to the interaction of higher-valent niobium species in the melt with the metal film. A more productive approach to Nb deposition involves prior chemical reduction to lower valence states, followed by electrochemical reduction to form Nb-Al films.

In the AlCl_3 : n-butyl-pyridinium chloride molten salt system, chemical reduction with aluminum powder allowed deposition of Nb-Al films with considerable niobium content [77]. Addition of aluminum powder to a solution of NbCl_5 eliminates the first two reduction processes mentioned above, producing a broadly spaced redox process at +0,6 V which seems to involve the +2 valence state. Electrodeposition at the aluminum reduction process in this melt was found to give a film containing up to 3 atomic% Nb.

Continuing studies of niobium electrodeposition involved reduction of low-valent niobium species in the aluminum chloride: EMIC melt. It had been determined earlier that reduction of Nb(V) species did not result in co-deposition of significant amounts of niobium in aluminum films deposited from the acidic melt. Addition of aluminum powder to Nb(V) solutions enabled deposition of slightly more niobium; however, aluminum is capable of reducing niobium to the zero-valent state and proved unreliable in forming consistent amounts of low-valent niobium species. A similar approach using niobium powder proved successful in forming Nb(III) species, the reduction of which resulted in niobium contents of 10-12% in the co-deposited Nb-Al films.

The general behavior reported by Hussey is the reversible step-wise reduction to Nb^{3+} . The formation of lower oxidation states results in dimerization and cluster formation. Metal-metal bonded chloride clusters having a $(\text{Nb}_6\text{Cl}_{12})^{z+}$ ($z = 1$ to 4) core have in fact been synthesized and examined in both basic and acidic AlCl_3 -EMIC room temperature melts [78].

In work of Barbato preliminary niobium deposition experiments showed that a thin layer of niobium deposit could be achieved from 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{BMP}]\text{Tf}_2\text{N}$) containing 0,25M NbF_5 and 0,25M LiF at 100°C under 1 hour, however further electrochemical experiments are required to improve the electrochemical parameters in order for a uniform, adherent layer of niobium to be obtained [15].

3. Experimental part

3.1. Introduction

This section describes the materials and the experimental set-up used in the current work. Electrochemical measurement techniques such as cyclic voltammetry, potentiostatic polarization and microstructural characterization techniques such as scanning electron microscopy (SEM), energy-dispersive x-ray analysis (EDX) and x-ray diffraction (XRD) are also presented.

3.2. Materials and chemicals

The electrodeposition of niobium was studied in the water and air stable ionic liquid 1-ethyl-3-methylimidazolium chloride (EMIC) purchased from Fluka (Assay $\geq 93\%$, $H_2O \leq 0,5\%$) and ABCR GmbH (Assay $\geq 97\%$) and 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIPF₆) purchased from Fluka (Assay $\geq 97\%$,). NbCl₅ (99%) was purchased from Sigma-Aldrich. Copper and Stainless steel substrates were used as working electrodes for electrochemical measurements. Niobium (Nb) wires was immersed in solution and applied as the quasi-reference (RE). Niobium and graphite rods were applied as the counter (CE) electrodes. It is critical to keep in mind from herein that all results are based on a quasi-reference electrode and not a true reference electrode.

3.3. Apparatus and procedures

3.3.1. Solutions and samples preparing

1-ethyl-3-methylimidazolium chloride (EMIC) and 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIPF₆) are yellowish color salts which have melting points 77-79°C and 58-62°C, respectively (Figure 3.1).



Figure 3.1: *1-ethyl-3-methylimidazolium chloride*

These salts became liquid even at room temperature just in contact with air. Besides NbCl_5 salt (Figure 3.2), which have been used like Nb ions source not stable in air atmosphere and solutions slowly decompose in air. For avoiding air contact was used closed system with nitrogen atmosphere (Figure 3.3).

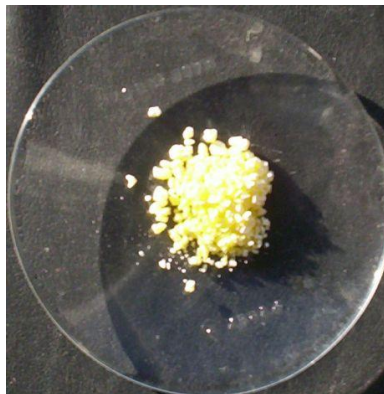


Figure 3.2: *Niobium pentachloride (yellow portion) that has partially hydrolyzed (white material)*

Electrochemical experiments were performed using a 50 cm^3 cell. Salt was put on the bottom of baker and was placed on heater and was heated slowly to temperature $150\text{-}200^\circ\text{C}$. It is necessary to keep melt at temperature higher 100°C for the evaporation of residual water.

Sample size is 8 cm lengths and 1 cm width. Samples were pulled down in a $1/4$ of length inside solution. Cleaning of samples was in next order:

- washing with soap (Rodaclean) and scotch-bright;
- washing in ultrasound with soap (Rodaclean);
- washing in ultrasound with deionized water;
- rinsing with deionized water;
- drying with alcohol and acetone using nitrogen blowing.

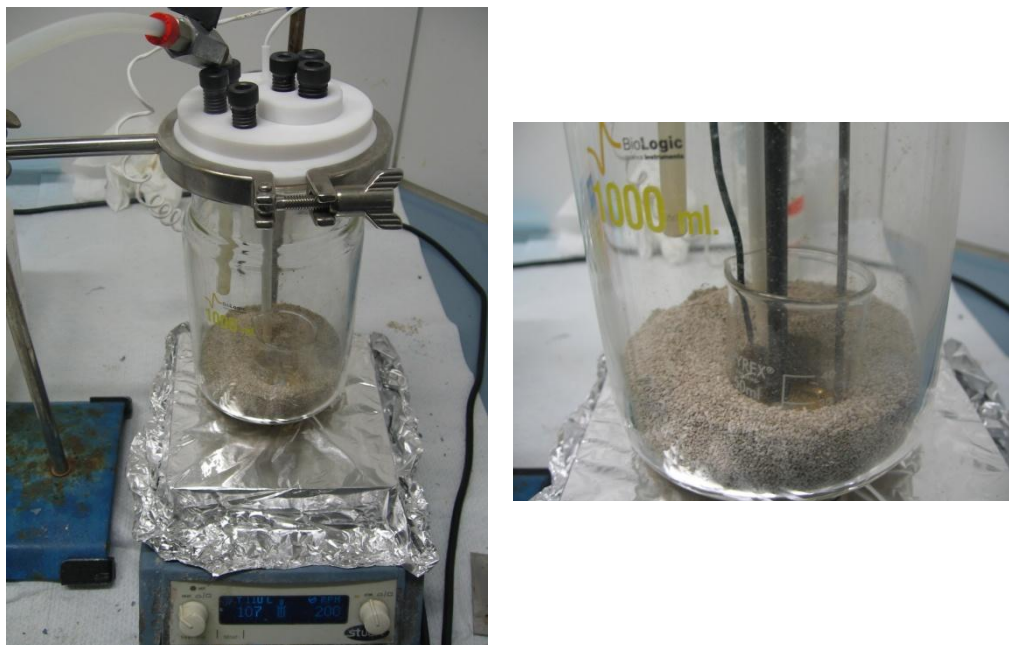


Figure 3.3: *Three-electrode electrochemical cell*

3.3.2. Potentiostat instrumentation

All experiments were carried out potentiostatically using a BioLogic SP-150 potentiostat connected to a PC for data acquisition and control.

A potentiostat is an instrument that provides the control of the potential difference between the working electrode and the reference electrode. The potentiostat implements this control by applying current into the cell between the working electrode (WE) and the counter electrode (CE) until the desired potential between the working electrode and the reference electrode (RE) is reached. Figure 3.4 shows the schematic diagram of a potentiostat with computer control.

In an electrochemical cell for electrodeposition, the working electrode is the electrode to be plated. A well-working reference electrode should have a constant electrochemical potential. In this work Nb wire using like a RE. It is not the best reference but is simple and it is enough to understand kinetic of process. The counter electrode completes the cell circuit. In this work graphite rod and niobium rod were used like CE. Working electrodes for this work were made from copper and stainless steel sheets with surface area 4 cm^2 .

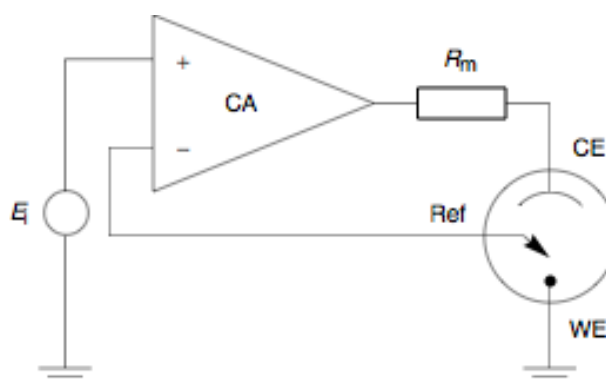


Figure 3.4: Schematic diagram of a potentiostat

3.3.3. Three-electrode system

3.3.3.1. Voltammetry

Electrode reactions are assumed to induce deviations from equilibrium due to the passage of an electrical current through an electrochemical cell causing a change in the working electrode potential. This electrochemical phenomenon is referred to as polarization. In this process, the deviation from equilibrium causes an electrical potential difference between the polarized and the equilibrium (unpolarized) electrode potential known as overpotential (η) [79].

Polarization is measured as overpotential, i.e. as a change in potential from the equilibrium half-cell electrode potential or the corrosion potential. During a linear sweep voltammetry scan the potential on the working electrode is varied linearly with the time and the change in current is recorded. Figure 3.5 shows a typical linear sweep voltammogram.

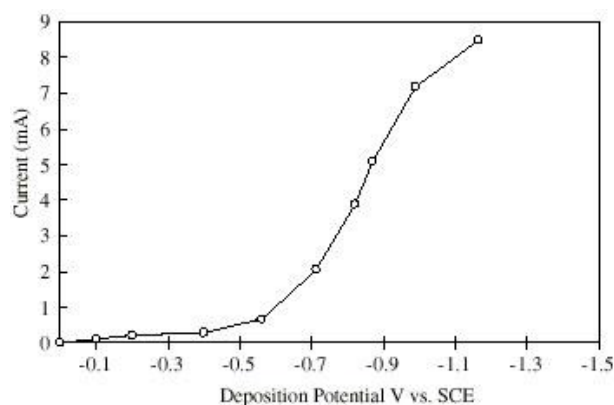


Figure 3.5: Schematic diagram of a linear sweep voltammogram

As can be seen at potential -0.5V vs. saturated calomel electrode (SCE) it started cathodic reaction which are increasing current. At higher overvoltage (potential close to -

1,2V) there is plateau, which means that current has limitation because of diffusion ions in electrolyte.

In order to understand what is happening on surface of samples in EMIC and EMIPF₆ melts were made linear sweep voltammetry and cyclic voltammetry tests in the solutions with different working electrodes. Cyclic voltammetry is faster than linear sweep voltammetry so it gives possibility to observe what is going on and at which potential region. Linear sweep voltammetry are slow but show what kinetic regime is defining the process what is the speed of process in all potential range. Linear sweep voltammetry and cyclic voltammetry were performed at a different scan rate at 70-200°C. The ionic solution was magnetically stirred immediately prior to each scan to avoid ion concentration gradients in the electrolyte. Stirring during the scan was avoided since it caused interference with the electrodes in the solution as only a small amount of ionic liquid was used at a time.

3.3.3.2. Electrodeposition process

Copper and stainless steel working electrode was used for electrodeposition. Furthermore, NbCl₅ was added to the ionic liquid and stirred until dissolved at different temperatures. In another experiments Nb ions were placed in ionic liquid by anodic dissolution. A cyclic scan was then performed to study the behavior of the liquid containing the Nb ions.

Potentiostatic scans were performed at various potentials for different time intervals to test deposition conditions. Between each potentiostatic scan, the sample was removed from solution and cleaned. The sample was washed in water, rinsed in distilled water and dried. The sample was then analyzed through an optical microscope to detect any deposits. Potentiostatic scans were repeated at different potentials until deposition was observed.

3.4. Surface and structure analysis

Upon completion of the electrodeposition process, various analytical techniques such as scanning electron microscopy, energy-dispersive x-ray analysis and x-ray diffraction were used to study the deposited layer on the substrate.

3.4.1. Scanning electron microscopy

Scanning electron microscopy (SEM) (Philips XL30) was used to investigate the surface morphology of the deposited film and energy dispersive X-ray analysis (EDX) was used to determine the film composition. The working distance for the EDX measurements was 10 mm between the objective lens and the specimen.

3.4.2. X-Ray diffraction

The 4 cm² samples were placed onto a low background silicon sample holder and run on an automated PANalytical X'Pert tube PW 3373/10 diffractometer. The system is equipped with a high power line focus Cu K- α source operating at 40 kV/40 mA. The diffraction patterns were collected on a $\theta/2\theta$ reflection geometry with fixed slits. A step scan mode was used for data acquisition with step size of 0,02° 2θ and counting time of 2,75 seconds per step. The preliminary qualitative phase analysis was performed by PANalytical data processing software X'Pert HighScore v.1.0f.

4. Experimental results and discussion

4.1. Solution

The molten salt was prepared by slowly mixing NbCl_5 and EMIC or EMIPF₆ with stirring until the desired molar ratio was obtained. The NbCl_5 like AlCl_3 Lewis acid made a deep eutectic with imidazolium salts, so during the mixing compositions have been started to melt. For removing all water impurities by evaporation melts were heated higher than 100°C. Also for avoiding problems with crystallization of salts on the surfaces of electrodes and to achieve low viscosity melts were heated to 190-200°C.

Another method to obtain ions of Nb in solution was anodic dissolving of pure Nb. Niobium rod was used like counter electrode and during experiments was observed its dissolution.

4.2. Voltammetry

The principal method for investigating the current potential dependence of an electrode–electrolyte system is cyclic voltammetry. A potentiostat is used to scan the potential with a constant scan rate ν (given in V/s or mV/s) from potential E_1 to potential E_2 . Then the scan direction is turned around and the associated current is measured. At potentials where an electrochemical process can occur characteristic peaks are observed (Fig. 4.6). Peak potential, peak height, and peak width are characteristic parameters. A big advantage of cyclic voltammetry is the detection of surface processes like adsorption, oxide layer formation, etc.

The cyclic voltammetry and linear sweep voltammetry was measured by a three-electrode system in a glass cell. Niobium, copper and stainless steel 316L were used as the working electrode, and an Nb (99,999%) rod or graphite rod were used as the counter electrode. An Nb wire (99,999%, \varnothing :1 mm) immersed in working melt was used as a reference electrode. The voltammetry measurements were carried out using a potentiostat BioLogic SP-150 connected to a PC for data acquisition and control.

The high temperature of melts make problem for using reference electrodes which usually applies in room-temperature aqueous solutions. For all potentiostatic and potentiodynamic experiments Nb wire immersed in electrolyte was used as reference electrode. It is showed very stable reproducibility of potentials during all experiments.

The electrochemical behavior of niobium (V) in different ionic liquids was investigated in respect to electrochemical deposition of niobium at the temperatures below 250°C.

4.2.1. Voltammetry of pure organic molten salts

To determine the purity level of the as-received salt, cyclic voltammetry and linear sweep voltammetry was performed. The types of impurities that could exist in the studied salts are halides and water. The exact impurities in the salts are unknown.

Figure 4.1 and 4.2 show the linear sweep voltammograms of stainless steel 316L electrode in EMIC and EMIPF₆ molten salts. The cathodic peak around -0,2...-0,4V vs. quasi-Nb was ascribed to the reduction of impurities such as HCl₂⁻ and H₂Cl₃⁻.

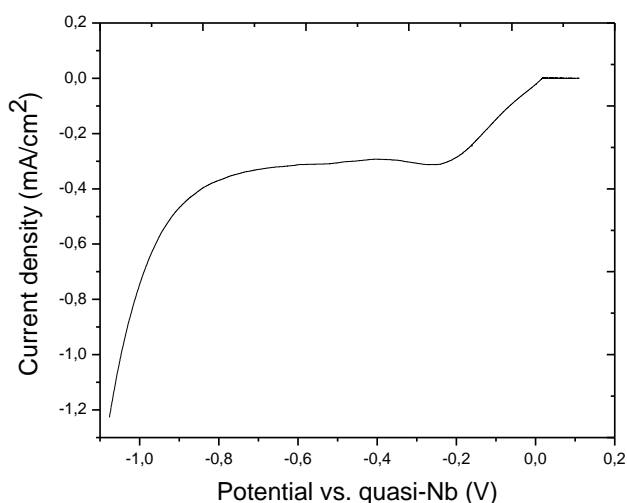


Figure 4.1: *Linear sweep voltammogram of stainless steel 316L electrode in EMIC molten salt at a sweep rate of 5 mV/s and temperature 185°C (Counter electrode – niobium rod)*

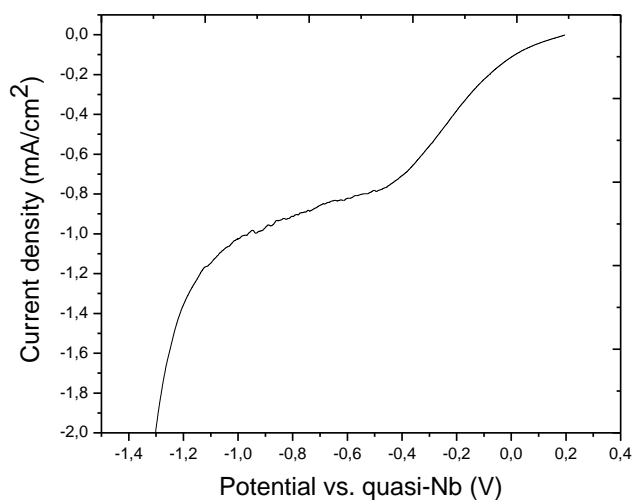


Figure 4.2: *Linear sweep voltammogram of stainless steel 316L electrode in EMIPF₆ molten salt at a sweep rate of 20 mV/s and temperature 150°C (Counter electrode – niobium rod)*

The reaction of impurities reduction has less overvoltage on stainless steel electrode than on niobium and starts with more positive potential (Fig 4.3).

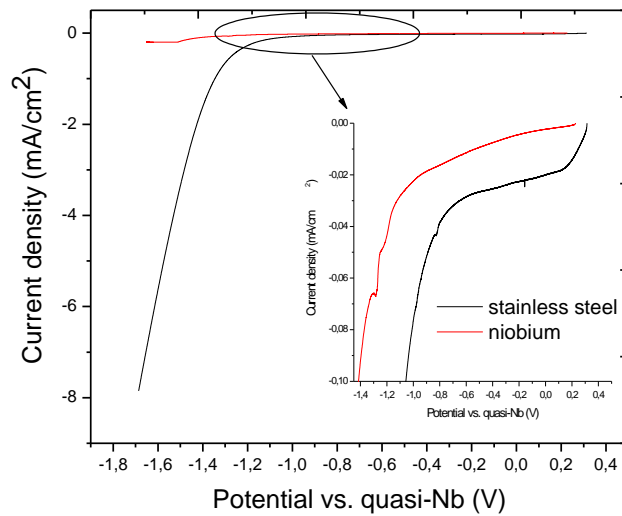


Figure 4.3: *Linear sweep voltammograms of stainless steel 316L and niobium electrodes in EMIPF₆ molten salt at a sweep rate of 20 mV/s and temperature 108°C (Counter electrode – graphite rod)*

For removing these impurities was used pre-electrolysis of electrolytes. In this case copper working electrode with surface area 4 cm² was chosen. As counter electrode was used niobium rod. The pre-electrolysis involves holding the potential while decreasing the overall current through the liquid. After potentiostatic holds at -0,8V (vs. quasi-Nb) for 8 hours (current density 0,65 mA/cm²), in a single quantity of ionic liquid (20 mL) on the surface of copper sample was observed uniform gray thin film (Fig. 4.5). Niobium anode during this process was dissolved. The color of electrolyte was changed from yellow to brown what can be evidence of niobium (IV) ions in solution (NbCl₄ – salt with brown color). After pre-electrolysis was obtained linear sweep voltammogram with new two peaks: one at -0,75V (P_2), another at -1,3V (P_3) (Fig. 4.6).



Figure 4.5: *Thin gray film on copper sample after pre-electrolysis in EMIC molten salt at -0,8V vs. quasi-Nb. (Counter electrode – niobium rod)*

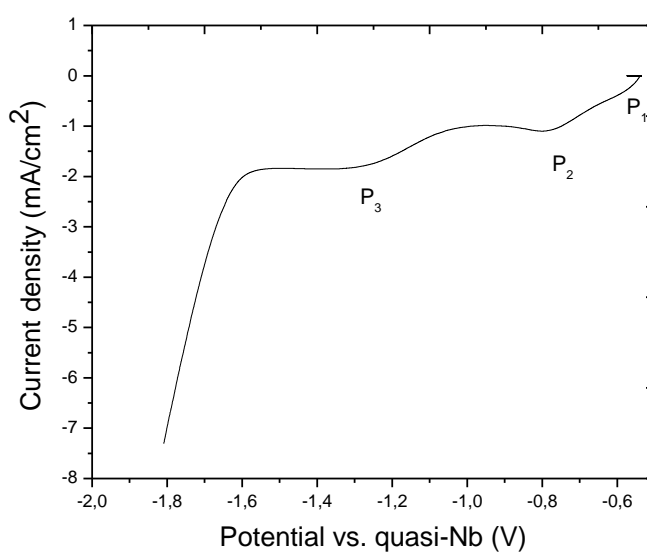


Figure 4.6: *Linear sweep voltammogram of copper electrode in EMIC molten salt at a sweep rate of 5 mV/s and temperature 192°C (Counter electrode – niobium rod)*

The second pre-electrolysis process with the same working parameters was done and was obtained the same thin film with metallic-gray color. The potentiostatic experiment with constant potential -1,2V for 7 hours shows another result. The color of thin film on copper sample became brown (Fig. 4.7), the color of melt was changed to black, which can be explained by reduction of niobium ions to Nb^{3+} (NbCl_3 – salt with black color).



Figure 4.7: *Thin brown film on copper sample after potentiostatic experiment in EMIC molten salt at -1,2V vs. quasi-Nb. (Counter electrode – niobium rod)*

Next potentiostatic experiments at potential -0,7V shows the corrosion of copper surface in the melts and films weren't observed. Experiments with graphite rod as counter electrode showed corrosion of copper samples even during first pre-electrolysis of new pure melt of EMIC and EMIPF₆. The working electrode was changed on stainless steel 316L.

On the surface of stainless steel sample during potentiostatic experiments in EMIC molten salt with potential -0,2V after 26 hours was obtained many-colored thin films with blue, yellow and colors which very similar to colors of niobium oxides (Fig. 4.8).

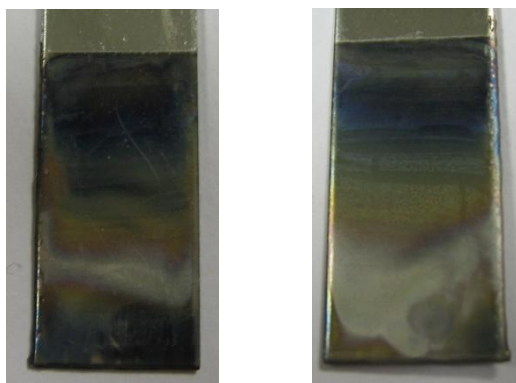


Figure 4.8: *Thin film on stainless steel sample after potentiostatic experiment in EMIC molten salt at -0,2V vs. quasi-Nb. (Counter electrode – niobium rod)*

During the electrolysis electrolyte became black. The incidental reduction reaction of gas on the cathode was observed. After running through the electrolyte 50 mAh quantity of electricity were obtained uniform thin films with black color (Fig. 4.9).

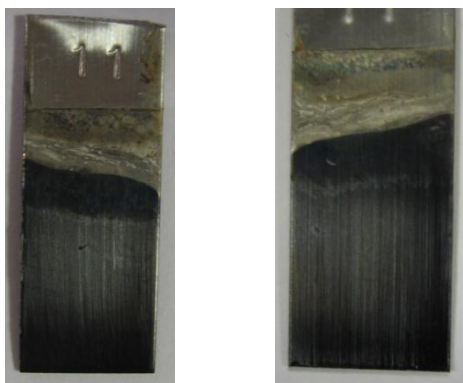


Figure 4.9: *Thin film on stainless steel sample after potentiostatic experiment in EMIC molten salt at -0,2V vs. quasi-Nb. (Counter electrode – niobium rod)*

4.2.2. Influence of different factors on the electrochemical processes

The influence of the following factors on the mechanism of electrochemical reduction was investigated:

- concentration of Nb^{5+} -ions;
- anionic composition of ionic liquids;
- temperature;
- different scan rate;
- material of working electrode.

4.2.2.1. Addition of NbCl_5 in molten salt

Figure 4.10 and 4.11 show a cyclic voltammograms of niobium and stainless steel in EMIPF_6 with and without containing of NbCl_5 .

Electrochemical reduction of NbCl_5 in melt shows a well-defined one-electron cyclic voltammetric process (P_1), followed by further reduction in a more complicated process, predominantly to the trivalent state (P_2 , P_3). Further reduction to the metallic state evidently does not occur, because a stripping peak for niobium oxidation is not observed even with a negative-going scan.

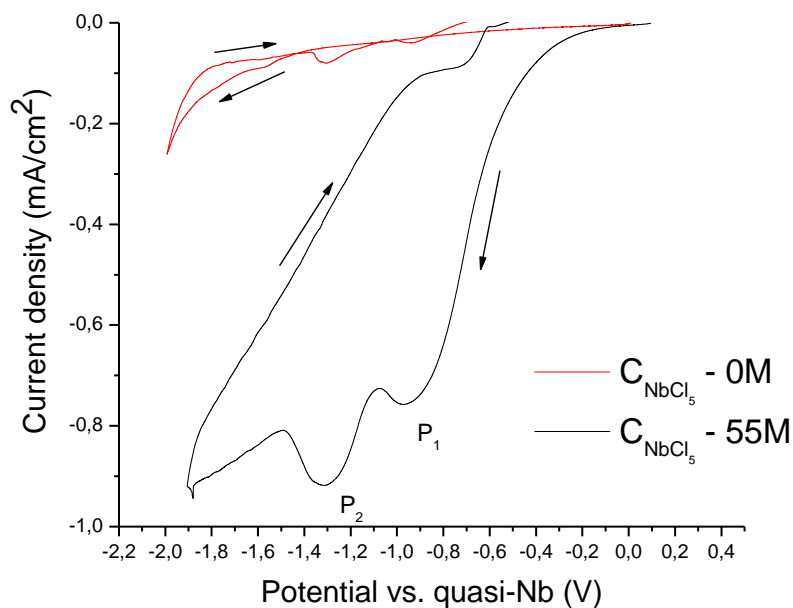


Figure 4.10: Cyclic voltammograms of niobium electrode in EMIPF_6 molten salt containing 0 and 55M NbCl_5 at a sweep rate of 20 mV/s and temperature 110°C (Counter electrode – graphite rod)

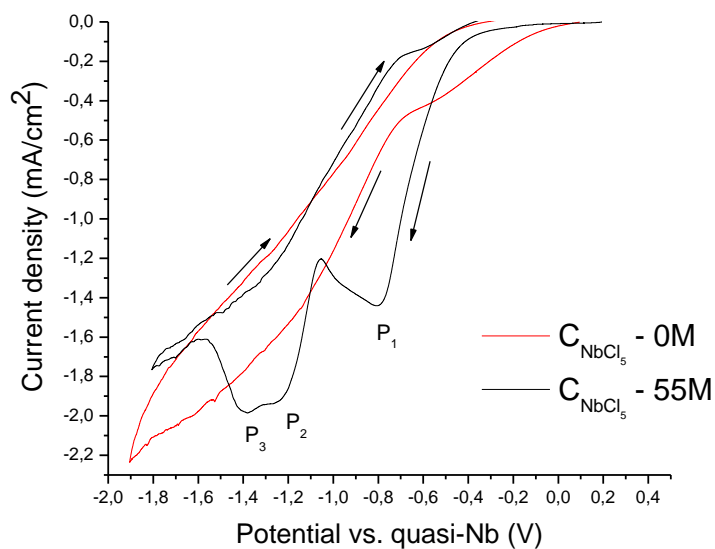


Figure 4.11: Cyclic voltammograms of stainless steel 316L electrode in EMIPF_6 molten salt containing 0 and 55M NbCl_5 at a sweep rate of 20 mV/s and temperature 110°C (Counter electrode – graphite rod)

4.2.2.2. Concentration of Nb^{5+} -ions

A few series of ionic liquids were obtained with the salt of niobium (V), namely NbCl_5 : the mixtures with 1-ethyl-3-methylimidazolium chloride (5,1 wt.% NbCl_5 – 95,9 wt.% EMIC; 16,7 wt.% NbCl_5 - 83,3 wt.% EMIC; 64,3 wt.% NbCl_5 – 35,7 wt.% EMIC) and 1-ethyl-3-methylimidazolium hexafluorophosphate (3,8 wt.% NbCl_5 – 96,2 wt.% EMIC).

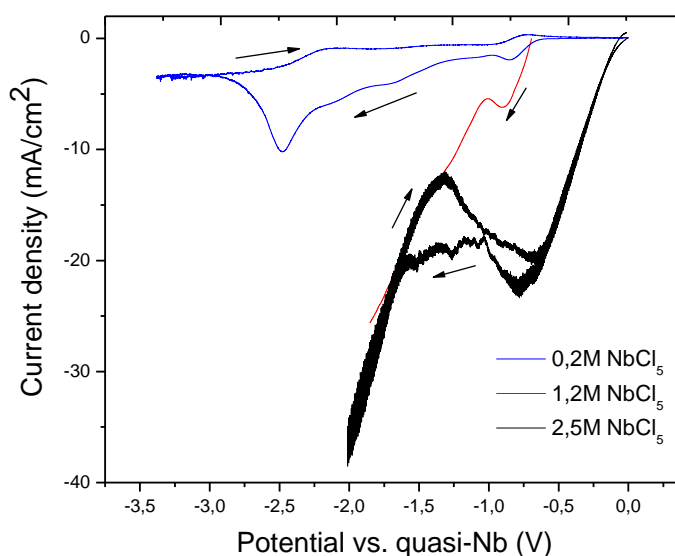


Figure 4.12: *Cyclic voltammograms of niobium electrode in EMIC molten salt containing different amount of NbCl_5 at a sweep rate of 20 mV/s (Counter electrode – graphite rod)*

Increasing of Nb^{5+} -ions concentration increases the current density of reduction processes to lower valent state (Nb^{4+}) and shifts potential of reaction in more positive side (Figure 4.12).

The same situation when Nb^{5+} -ions were added in solution by anodic dissolution. The rate of reduction process increases with the increasing of niobium ions concentration (Figure 4.13).

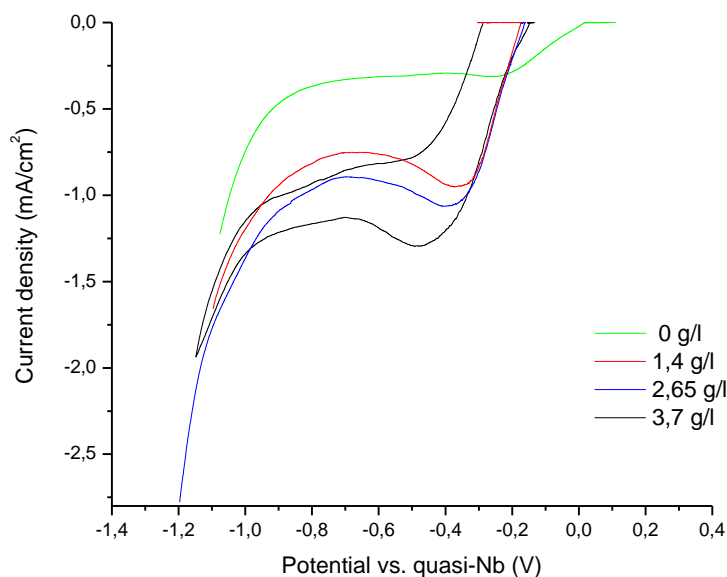


Figure 4.13: Cyclic voltammograms of stainless steel 316L electrode in EMIC molten salt with different concentration of Nb ions obtained by anodic dissolving. A sweep rate is 5 mV/s and temperature 180-185°C (Counter electrode – niobium rod)

4.2.2.3. Anionic composition of ionic liquids

Organic molten salts which were used as solvents for NbCl_5 have two different anions – Cl^- and PF_6^- . In melt of EMIPF₆ niobium anode was dissolved easier than in EMIC. Graphite counter electrode was stable in EMIC melt but failed in EMIPF₆. Figure 4.14 shows that in EMIPF₆ potential of peaks more positive than in EMIC. Probable the hexafluorophosphate-ions make with Nb-ions less stable complexes and overvoltage of reduction of these complexes lower.

Addition NaF and KF in electrolytes of EMIC and EMIPF₆ with NbCl_5 didn't change the polarization curves because of low dissolubility of these salts in present ionic liquids.

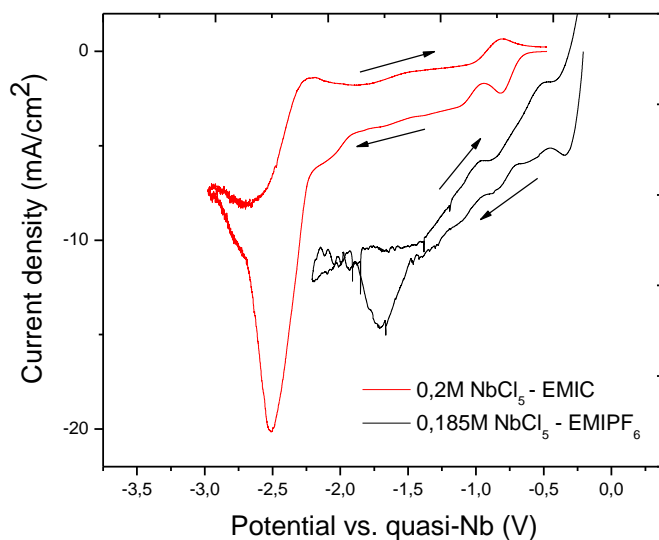


Figure 4.14: *Cyclic voltammograms of stainless steel electrode in EMIC and EMIPF₆ molten salts containing NbCl₅ at a sweep rate of 20 mV/s (Counter electrode – graphite rod)*

4.2.2.4. Temperature

As seen from Figure 4.15. increasing of temperature of solution increases the rate of processes. It is can be explain by increasing of diffusion coefficient which means that process limited by diffusion stage.

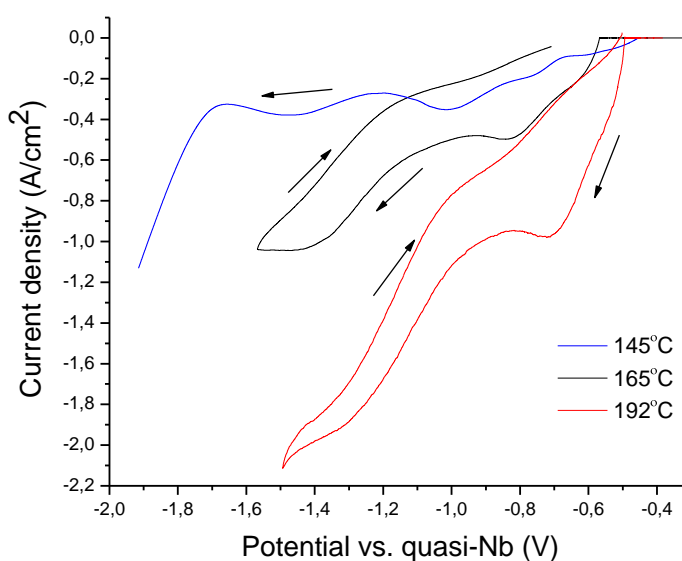


Figure 4.15: *Cyclic voltammetry on copper in EMIC melt with different temperature of solution*

4.2.2.5. Different scan rate

The cathodic peak around -0,6 V was assigned to the reduction of pentavalent niobium species, NbCl_6^- . The peak potential shifted to more negative side with increase in the scan rate, indicating that the reduction process is electrochemically irreversible.

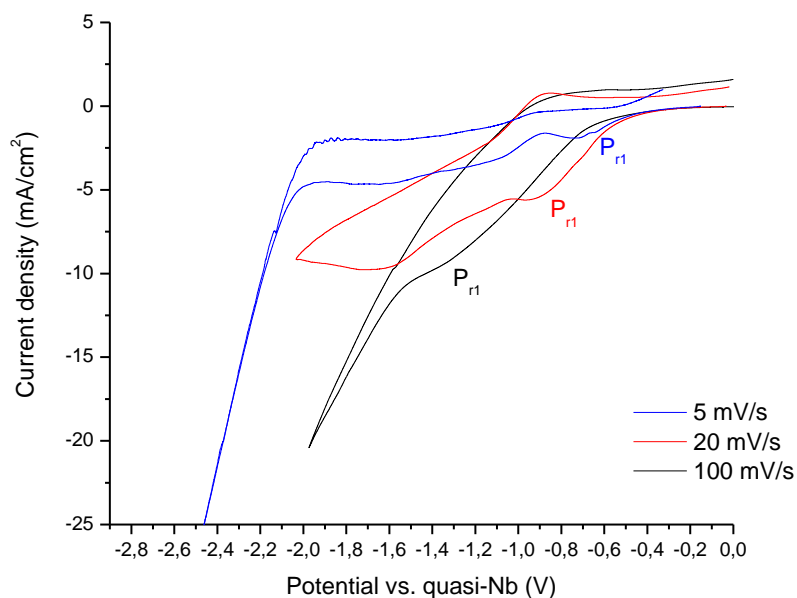


Figure 4.16: Cyclic voltammograms of niobium electrode in EMIPF_6 molten salt containing 55M NbCl_5 at a different scan rate and temperature 110°C (Counter electrode – graphite rod)

4.2.2.6. The material of working electrode

Figure 4.17 shows that on niobium occurs two reduction processes as opposite to copper metal. The reduction of Nb ions to lower valency seems to occur catalytically on niobium electrode while it is not observed on copper electrode, suggesting the reduction mechanism involves some chemical adsorption processes on the niobium electrode.

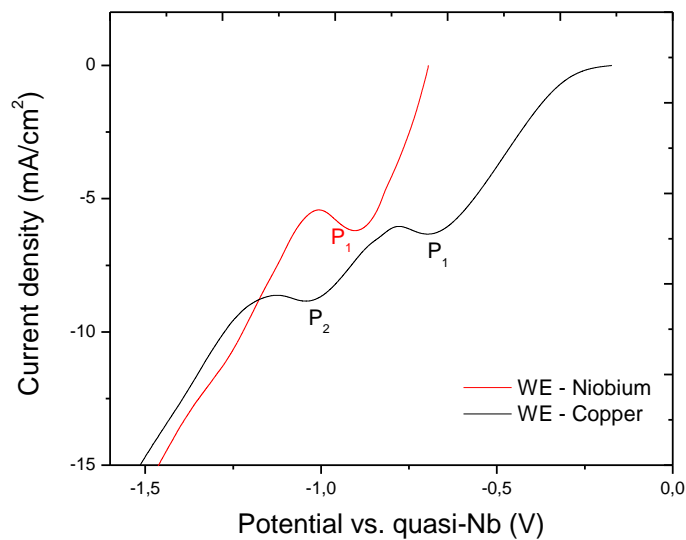


Figure 4.17: Cyclic voltammograms of copper and niobium electrode in EMIC molten salt containing 1,2M NbCl₅ at a sweep rate of 20 mV/s at temperature 75°C (Counter electrode – graphite rod)

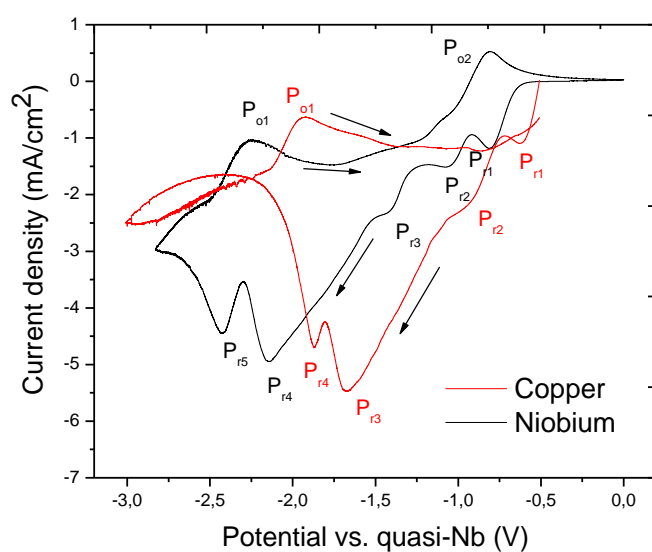


Figure 4.18: Cyclic voltammograms of copper and niobium electrode in EMIC molten salt containing 0,2M NbCl₅ at a sweep rate of 20 mV/s at temperature 75°C (Counter electrode – graphite rod)

4.3. Surface analysis

To determine whether or not the electrodeposit contained crystalline niobium, x-ray diffraction patterns (XRD) were acquired. The XRD patterns of the initial deposits showed only the characteristic patterns of the copper and stainless steel substrates and no evidence for crystalline niobium. This meant that the electrodeposits were either amorphous or so small in their crystal size that within the resolution of the device, no XRD peaks could be obtained.

5. Conclusions

In this work different main things were determined/proofed:

1. NbCl_5 as a Lewis acid makes with organic salts based on imidazolium ions deep eutectic with melting point less than room-temperature.
2. Voltammetry analysis shows a behavior of Nb^{5+} ions. There are two one-electron steps of Nb^{5+} ions reduction to Nb^{4+} and than to Nb^{3+} . Increasing of Nb^{5+} -ions concentration increases the current density of reduction processes to lower valent state (Nb^{4+}) and shifts potential of reaction in more positive side. The same situation when Nb^{5+} -ions were added in solution by anodic dissolution. The rate of reduction process increases with the increasing of niobium ions concentration.
3. Increasing of temperature of solution increases the rate of processes. It is can be explain by increasing of diffusion coefficient which means that process limited by diffusion stage.
4. During the electrolysis of EMIC molten salt with Nb ions which were inputted in solution by anodic dissolution of niobium metal were obtained uniform thin films with gray color on copper substrates and many-colored (blue-yellow-red) and black films on stainless steel. The XRD patterns of the initial deposits showed only the characteristic patterns of the copper and stainless steel substrates and no evidence for crystalline niobium. This meant that the electrodeposits were either amorphous or so small in their crystal size that within the resolution of the device, no XRD peaks could be obtained.
5. Obtained films could be used as decorative and corrosion protective films for different metals.

6. Future work

- The present work has shown that it is possible to deposit uniform thin films from an ionic liquid with niobium ions.
- The immersion and corrosion tests should be performed on the coated samples to test the protective properties of films.
- Another issue which also attracts an attention is performing the analysis of surface with SEM and EDAX.
- Also it would be interesting to build a new reference electrode that could be completely stable in the ionic liquid used in this study.

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