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Spectroscopic study of the electrochemical behaviour of tantalum(V) chloride and oxochloride species in 1-butyl-1-methylpyrrolidinium chloride

Olga B. Babushkina*,[1], Silvia Ekres

Centre in Electrochemical Surface Technology (CEST), Viktor Kaplan street 2, A-2700, Wiener Neustadt, Austria

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ABSTRACT

FTIR spectroscopy was used to identify the oxochloride species of tantalum(V) in ionic liquids and to confirm the correlations between their presence in electrolytes and the changes in the route of electrochemical reduction of tantalum(V). Electrochemical behaviour of the mixtures (x)1-butyl-1-methyl-pyrrolidinium chloride-$(1-x)$TaCl$_5$ at $x = 0.80$, 0.65, and 0.40 was investigated over the temperature range 90–160 °C with respect to the electrochemical deposition of tantalum and was discussed in terms of spectroscopic data. The mechanism of electrochemical reduction of tantalum(V) in the basic and acidic electrolytes depends strongly on the structure and composition of the electro active species of tantalum(V) defined by the molar composition of ionic liquids and on the competition between tantalum(V) chloride and oxochloride species. In the basic mixture at $x = 0.80$, with octahedral $[TaCl_6]^-$ ions as the electrochemically active species only the first reduction step $Ta^{5+} \rightarrow Ta^{4+}$ at −0.31 V was observed. The competitive reduction of tantalum(V) oxochloride species occurs at more anodic potential (−0.01 V) than the reduction of the chloride complexes and can restrict the further reduction of tantalum(IV). In the basic ionic liquid at $x = 0.65$, the cyclic voltammograms exhibit reduction peaks at −0.31 V and −0.51 V attributed to the diffusion controlled process as $[TaCl_6]^- + e^- \rightarrow [TaCl_6]^{2-}$ and $[TaCl_6]^{2-} + e^- \rightarrow [TaCl_6]^{3-}$. The further irreversible reduction of tantalum(III) to metallic state may occur at −2.1 V. In the acidic ionic liquids, at $x = 0.40$ the electrochemical reduction of two species occurs, $TaCl_6^-$ and $Ta_2Cl_{11}^-$ and it is limited by two electron transfer for both of them at −0.3 V and −1.5 V, respectively.

1. Introduction

Electrochemical deposition of refractory metals, particularly tantalum, can be achieved from non-aqueous electrolytes. Successful preparation of tantalum coatings depends on the composition of electrolyte, concentration of tantalum(V) salts, temperature and impurities of tantalum oxohalides. In high temperature molten salt electrolytes these effects are well defined. The tantalum electrodeposition from ionic liquids at lower temperatures, as an alternative media to high temperature molten electrolytes, avoids the thermal damage of substrate during the electrolysis and would promote the extension of its application range. The role of the factors mentioned above, especially the influence of tantalum(V) oxohalides on the route of electrochemical reduction of tantalum(V) from ionic liquids, is enhanced due to the much lower temperature of the electrolytic bath and the hygroscopic nature of ionic liquids. The lack of knowledge in this field initiated the present studies.

1.1. High temperature molten salt electrolytes

High temperature molten salts (molten alkali metal fluoride, chloride, and mixed chloride–fluoride systems) were found to be efficient baths for tantalum electrodeposition, since pure tantalum cannot be deposited in significant amounts from aqueous solutions and organic solvents. Alkali metal chloride electrolytes containing $TaCl_5$ are highly volatile and hygroscopic, but their melting points are about 500 °C and are lower than those of the alkali fluoride electrolytes. Numerous achievements on the electrochemical reduction of tantalum to metallic state from alkali chloride melts were reported [1–6]. Alkali metal fluorides containing K_2TaF_7 are not as volatile and hygroscopic as the chlorides, but they are considered to be toxic and corrosive. The most successful electrochemical depositions of tantalum were achieved from alkali metal fluoride electrolytes at temperatures above 700 °C [7–13]. Attempts were undertaken to optimize the composition of electrolytes using the mixed alkali metal chloride–fluoride electrolytes [14,15]. In general the disadvantage of the molten alkali chloride- and fluoride systems is the high operating temperatures at which the substrate can suffer thermal damage and structural changes, the increased corrosion rates of the cell material, etc.

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* Corresponding author. Tel.: +43 02622 22266 37; fax: +43 02622 22266 50.
E-mail address: olga.babushkina@cest.at (O.B. Babushkina).

[1] “ISE member”.

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Since the oxohalide complexes of tantalum(V) can perturb the electrochemical reaction and degrade the quality of the deposited metal, the purity of the electrolytic bath, especially the impurities of tantalum(V) oxohalides, is a crucial factor for tantalum deposition. A few studies were performed to investigate the formation of oxohalide species of tantalum(V) and their influence on the electrochemical behaviour of tantalum(V) in high-temperature electrolytes [3,9,10,12,14]. Investigating the influence of Na_2O addition on the formation of tantalum(V) species and on the mechanism of tantalum(V) reduction, Polyakova et al. [11] have found that depending on the molar ratio between oxide ions and K_2TaF_7, different fluoro and oxofluoride species are formed in the electrolyte. They claimed that both the fluoro complex $[TaF_7]^{2-}$ and the mono-oxofluoro complex $[TaOF_5]^{2-}$ can be reduced to metallic tantalum in a single five-electron step in the temperature range of 560–815 °C. The electrochemical reduction of the dioxofluoro complex $[TaO_2F_x]^{(x-1)-}$ leads to the formation of insoluble $KTaO_3$. Chamelot et al. [12] on the other hand, confirmed that only the reduction of oxygen-free complexes of tantalum(V) leads to the formation of metal. Thus, tantalum coatings can be obtained successfully from oxygen-free electrolytes or when the content of oxygen impurities in the electrolyte is negligibly low. When tantalum oxofluorides are present in the melt, their reduction leads to the formation of tantalum oxides, which prevent the deposition of metallic tantalum.

1.2. Ionic liquids

Since the first article on the electrochemistry of tantalum(V) in room temperature molten salts published by Barnard and Hussey in 1990 [16], there were many attempts of deposition of tantalum coatings from ionic liquids at temperatures below 200 °C.

A few studies have been published on the electrochemistry of tantalum(V) in different ionic liquids: 1) in imidazolium-based ionic liquids, 1-ethyl-3-methylimidazolium chloride (EMIC)-$AlCl_3$ [16], EMIC [17,18], and 1-ethyl-3-methylimidazolium hexafluorotantalate ($EMITaF_6$) [19]; and 2) in a pyrrolidinium-based ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ($Pyr_{14}TFSI$) [20–22] and in 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [23].

Barnard and Hussey [16] have studied the electrochemistry of $TaCl_5$ in $AlCl_3$-1-ethyl-3-methylimidazolium chloride (EMIC) ionic liquid at 40 °C and they reported the reduction of tantalum from state (V) only to state (III). Morimitsu et al. claimed to achieve metallic tantalum at 100 °C from a bath containing $TaCl_5$, EMIC, and LiF in 30:60:10 mol% ratios, respectively [17,18]. However, the X-ray diffraction (XRD) patterns of the deposits show besides tantalum an “unknown” element, which could be due to oxygen impurities. Zein El Abedin et al. [20–22] presented the results on the electrodeposition of tantalum on Au, Pt, and NiTi alloy substrates from the solution of TaF_5 in the ionic liquid 1-butyl-1-methylpyrrolidinium (Pyr_{14}^+) bis(trifluoromethylsulfonyl)imide (TFSI). They reported the deposition of tantalum at 200 °C; however the EDAX spectrum shows the presence of oxygen, together with carbon and sulfur, 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. This suggestion seems unconvincing because the reaction of tantalum with oxygen under the open atmosphere occurs under heating above 280 °C [24].

It must be said that the authors did not consider the formation of oxofluoride species of tantalum(V) in the electrolyte and overlooked the possibility that the additional reduction peaks could be due to the reduction of oxofluoride complexes of tantalum(V), resulting in the presence of tantalum oxide(s) in the deposited layer. Only Barnard and Hussey have used the treatment by phosgene gas to remove the impurities of tantalum(V) oxochlorides from ionic liquids [16].

In our article [23], the formation of mixed oxochloro and chloro-fluoro complexes of tantalum(V) was confirmed in ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate containing up to 35 mol% $TaCl_5$ by means of FTIR spectroscopy. As the content of $TaCl_5$ was increased, primarily $[TaOCl_4]^-$ complexes were found to be the dominant species in ionic liquids due to the preferable coordination by oxygen of the $CF_3SO_3^-$ group and the ionic liquids with oxygen-containing functional groups were considered unsuitable candidates for successful electrodeposition of tantalum coatings.

The present paper is devoted to the study of the electrochemical behaviour of tantalum(V) in basic ($x = 0.80$ and 0.65) and acidic ($x = 0.40$) $(x)Pyr_{14}Cl\text{-}(1-x)TaCl_5$ mixtures. The influence of tantalum(V) oxochloride species on the mechanism of electrochemical reduction of tantalum(V) species was confirmed on the base of FTIR spectroscopic data.

2. Experimental

2.1. Chemicals

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 h under high 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 using a Coulometer 756 KF (Metrohm) calibrated with Hydranal 100 ppm Water Standard (NIST SRM 2890 traceable) and was typically below 7–8 ppm.

$TaCl_5$ (mp 211 °C) purchased from Alpha Aesar (99.99%, packed in bottle) and $TaCl_5$ of Aldrich Chemical Company (99.999%, ampoule packed under argon) were used without preliminary purification.

Na_2O was prepared by heating of a mixture of sodium oxide and sodium peroxide (Aldrich, 80% Na_2O, containing < 20% Na_2O_2) at 600–650 °C in an alumina crucible under high vacuum until gas evolution ceased [25]. After the compound had been crushed in a glove box, this procedure was repeated once more.

2.2. Sample preparation

The mixtures $(x)Pyr_{14}Cl\text{-}(1-x)TaCl_5$ form liquids in a wide range of compositions at $x = 0.80$–0.30 under heating at different temperatures. The compositions for electrochemical studies ($x = 0.80$, 0.65, and 0.40) were prepared by combining $Pyr_{14}Cl$ with a corresponding amount of $TaCl_5$, mixed in the glove box (Mbraun Star, O_2 and H_2O content below 1 ppm), placed in Pyrex tubes, and melted in an inert atmosphere of argon (99.999%) in an oil bath with stirring until the liquids formed.

The mixtures $(x)Pyr_{14}Cl\text{-}(1-x)TaCl_5$ at $x = 0.65$ and 0.40 are the most easily formed transparent liquids: the first one is a light-yellow liquid formed at ~80 °C and the second one is colourless and formed at ~130 °C. At high concentration of $TaCl_5$ (60 mol%) some precipitation of white powder was observed on the walls of the tubes during the heating due to the partial volatility of $TaCl_5$.

To investigate the influence of the possible impurities of tantalum(V) oxochloride in the starting materials on the electrochemical behaviour of tantalum(V), the ionic liquids were prepared with $TaCl_5$ of different qualities (bottle packed and ampoule packed). The mixture $(x)Pyr_{14}Cl\text{-}(1-x)TaCl_5$ at $x = 0.65$ with Na_2O additive