Spectroscopy and Electrochemistry of Tantalum(V) in 1-Butyl-1-methylpyrrolidinium Trifluoromethanesulfonate

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FTIR spectroscopic and electrochemical characterizations of tantalum(V) in 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (Pyr$_{14}$TFMS)-TaCl$_5$ ionic liquids are performed with 5, 15, and 35 mol% TaCl$_5$ as the media for potential electrochemical application. On the basis of FTIR spectra the electrochemical active species are identified as follows: $[TaOCl_4]^-$, $[TaOCl_5]^{2-}$, $[TaCl_5F]^-$, and $[TaCl_5F_2]^{2-}$. The dominant species are the oxochloride complexes of tantalum(V).

Cyclic voltammograms of Pyr$_{14}$TFMS-TaCl$_5$ mixtures at 80 °C exhibit three reduction peaks: at -0.8 V, -0.9 V, and -2.4 V. The first reduction peak corresponds to the reduction of the oxochloride species of tantalum(V), the second is assigned to the reduction of the mixed chloride-fluoride species of tantalum(V), and the third peak to the further reduction of tantalum.

The spectroscopic data confirm the suggestion that oxochloride complexes of tantalum(V) become the dominant species in ionic liquids with the oxygen-containing functional group $[CF_3SO_3]^-$, possibly restricting the process of tantalum metal deposition from these ionic liquids.

Key words: Tantalum(V) Chloride; 1-Butyl-1-methylpyrrolidinium Trifluoromethanesulfonate;
Ionic Liquids; Spectroscopy; Electrochemistry.

1. Introduction

Electrochemical deposition of tantalum cannot be achieved from aqueous solutions or organic solvents. High-temperature molten salts (molten alkali fluorides, alkali chlorides and mixed alkali chloride-fluoride systems) were found to be efficient baths for tantalum electrochemical deposition. Alkali chloride electrolytes containing chlorides of refractory metals, particularly TaCl$_5$, are highly volatile and hygroscopic. However, the operating temperatures are relatively low (above 500 °C) – lower than those of the alkali fluoride electrolytes. The achievements in the reduction of tantalum(V) to the metal state from alkali chloride electrolytes were reported in [1 – 3].

Alkali fluoride electrolytes containing K$_2$TaF$_7$ are not as volatile and hygroscopic as alkali chlorides, but they are more corrosive to electrolytic baths and require operating temperatures above 700 °C. The most successful electrochemical deposition of tantalum was achieved from alkali fluoride electrolytes [4 – 7].

Low-temperature molten salts or ionic liquids are considered as promising alternative electrolytes for the electrochemical deposition of refractory metals. Their advantages over the high-temperature molten salts are their negligible vapour pressure, wide window of electrochemical stability, high thermal stability (up to 350 °C), and the fact that they are often liquid at room temperature. A few studies on the electrochemistry of tantalum(V) in different ionic liquids have been published [8 – 12]. Morimitsu et al. [9, 10] and Zein El Abedin et al. [11] have reported that tantalum deposition was achieved from ionic liquids. However, in all cases the X-ray diffraction patterns of the deposits show the presence of oxygen impurities.

The purity of the electrolyte, especially the absence of oxygen impurities, is a crucial factor for tantalum deposition as the oxohalide complexes of tantalum(V) can perturb the electrochemical reaction and degrade the quality of the deposited metal. A few studies have been performed to investigate the formation of tantalum(V) oxohalide species and their subsequent influ-

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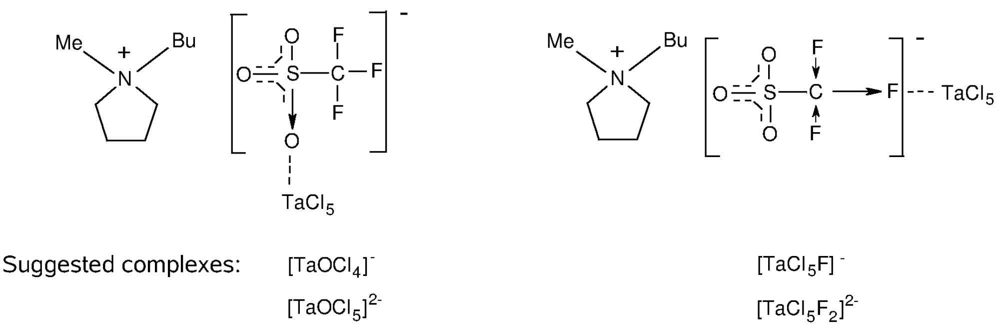


Fig. 1. Suggested complex formation in Pyr_{14}TFMS-$TaCl_5$ mixtures.

ence on the electrochemical behaviour of tantalum(V) in high-temperature electrolytes [5 – 7, 13]. In the case of electrochemical deposition of tantalum from ionic liquids Barnard and Hussey used phosgene gas to remove oxochloride impurities [8].

The identification of halide and oxohalide species of tantalum(V) in the electrolytes by means of spectroscopic methods provides important information about the tantalum(V) electrochemical reduction mechanism. The electrochemical and spectroscopic behaviour of $TaCl_5$ in the room-temperature ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (Pyr_{14}TFMS) was investigated with 5, 15, and 35 mol% $TaCl_5$. The structure and composition of tantalum(V) species formed in pyrrolidinium salts with the oxygen-containing functional group $[CF_3SO_3]^-$ was investigated, to confirm the suggestion of the formation of oxohalide species and to determine their influence on the applicability of these ionic liquids as electrolytes for the electrochemical deposition of tantalum.

2. Experimental

2.1. Chemicals and Sample Preparation

The ionic liquids consisted of Pyr_{14}TFMS as the organic and $TaCl_5$ as the inorganic component. The commercial Pyr_{14}TFMS (m. p. 3 °C, thermal stability up to 340 °C) was purchased from Merck. Pyr_{14}TFMS was dried under high vacuum (0.003 mbar) at 95 – 100 °C with intensive stirring for 48 h prior to use; after drying its water content, determined by Karl Fischer coulometric titration, was typically 6 – 7 ppm.

Ampoule-packed $TaCl_5$ (99.999%) was purchased from Alfa Aesar and used without preliminary purification.

The Pyr_{14}TFMS-$TaCl_5$ ionic liquids were prepared by combining stoichiometric amounts of Pyr_{14}TFMS and $TaCl_5$. The components were mixed in an MBraun Star glove box (content of O_2 and H_2O below 1 ppm), placed in Pyrex tubes and melted in an inert atmosphere of argon (99.999%). Three different compositions of Pyr_{14}TFMS-$TaCl_5$ at the molar ratios of the components 95 : 5, 85 : 15, and 65 : 35 were obtained at 50, 80, and 120 °C, respectively, after $\sim$ 3 h of intensive stirring.

2.2. Spectroscopic Measurements

FTIR spectra were recorded in the range 200 – 4000 cm^{-1} using a Bruker FTIR spectrometer Equinox 55 with an MKII Golden Gate single reflection ATR system with a diamond top plate, KRS-5 lenses (Specac, England), and a MCT nitrogen-cooled detector (64 scans).

2.3. Electrochemical Measurements

A Voltalab 40 model PGZ 301 potentiostat was used for electrochemical measurements with a tightly sealed three-electrode cell with inert argon atmosphere. The working electrode was a platinum disc (Pt wire, ∅ 0.5 mm, sealed in Duran), and the counter electrode was a glassy carbon rod (∅ 3 mm). A platinum wire was used as a quasi-reference electrode. The cyclic voltammograms were recorded at a scan rate of 0.1 V s^{-1}.

3. Results and Discussion

3.1. FTIR Spectroscopic Studies

In Pyr_{14}TFMS-$TaCl_5$ ionic liquids the formation of new $[TaCl_5X]^{n-}$ ($X = O^{2-}, F^-$) complexes is expected. One can suggest the participation of fluorine and oxygen from the $[CF_3SO_3]^-$ group of the pyrrolidinium salt in the formation of new tantalum(V) complexes according to the proposed scheme (Fig. 1).

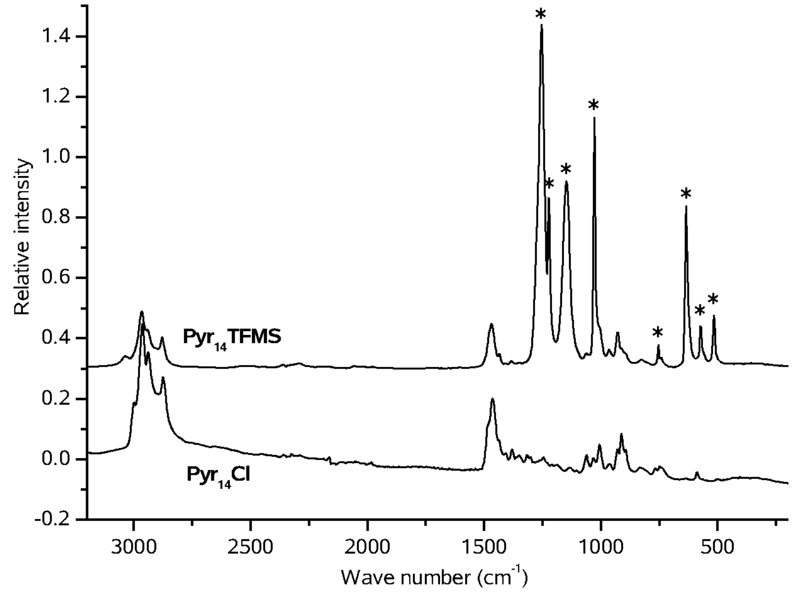


Fig. 2. FTIR spectra of Pyr$_{14}$TFMS and Pyr$_{14}$Cl; * vibrations of the $[CF_3SO_3]^-$ anion.

Table 1. Tentative assignment of the observed bands in the FTIR spectrum of Pyr$_{14}$TFMS.

Wave number (cm^{-1})[a]	Vibration	Species
3037 m	ν_{as}(CH)	Pyr$_{14}^+$
2967 m	ν_s(CH)	
2880 m		
1469 m	$\delta(CH_2)$	
1254 s	$\nu_{as}(SO_2)$	$[CF_3SO_3]^-$
1223 s	ν_{as}(CF)	
1148 s	ν_s(CF)	
1028 s	$\nu_s(SO_2)$	
965 vw	ring mode	Pyr$_{14}^+$
929 w		
913 vw		
898 vw		
825 vw		
755 w	$\delta_s(CF_3)$	$[CF_3SO_3]^-$
635 s	δ_s(OSO)	
572 m	$\delta_{as}(CF_3)$	
516 m	$\delta_{as}(CF_3)$ or δ_{as}(OSO)	

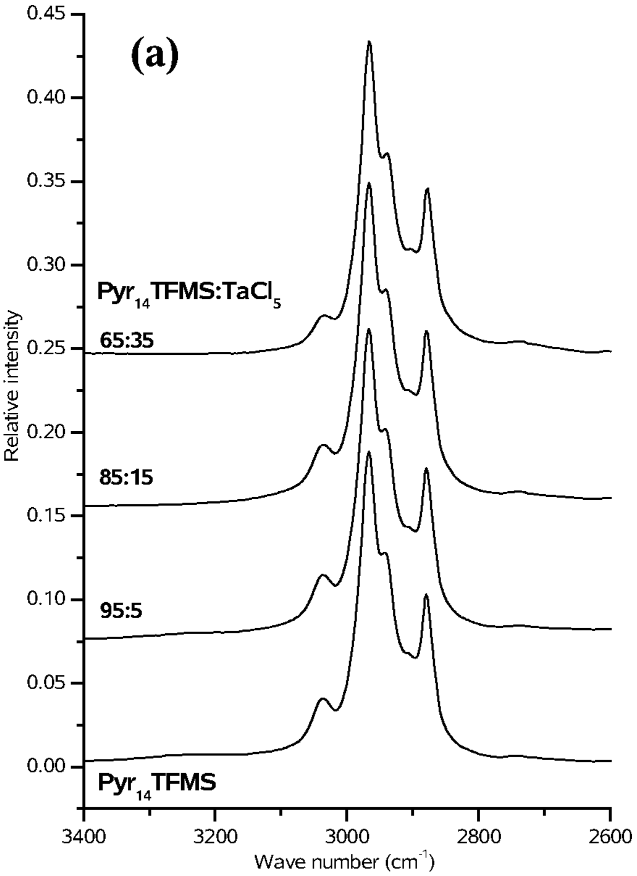
[a] m, medium; s, strong; w, weak; vw, very weak.

The assignment of the vibrational features of the pyrrolidinium ring in Pyr$_{14}$TFMS was done on the basis of comparison with the FTIR spectrum of Pyr$_{14}$Cl (Fig. 2) and the results reported for liquid pyrrolidine [14, 15] and different alkylpyrrolidinium salts [16, 17]. The identification of the vibrations of the $[CF_3SO_3]^-$ group in Pyr$_{14}$TFMS was done on the basis of data for CF_3SO_3H [18], $LiCF_3SO_3$ in acetonitrile [19] and $CF_3SO_2OSiH_3$ [20]. The tentative assignment of the vibrations of Pyr$_{14}$TFMS is summarized in Table 1.

The intensities of the vibrational features of $[CF_3SO_3]^-$ groups (marked with asterisks in Fig. 2) were significantly higher than those of the pyrrolidinium ring; thus it was quite complicated to estimate the inter-ionic interaction in Pyr$_{14}$TFMS. Single-crystal X-ray diffraction data of *N*,*N*-dimethylpyrrolidinium bis(trifluoromethanesulfonyl) amide (TFSA) [21] showed this salt to consist of discrete ions with only weak C-H...O contacts between the constituent atoms of cations and anions close to the limits of van der Waals separations. The closest approaches of the cation and anion are between the sulfonyl oxygen atoms and C-H bonds on the cations.

FTIR spectra of Pyr$_{14}$TFMS and Pyr$_{14}$TFMS-$TaCl_5$ mixtures at various molar ratios of components are presented in Figure 3. In the spectra of Pyr$_{14}$TFMS-$TaCl_5$ mixtures new vibrational features were observed at 501, 596, 928, 969, 1203, and 1368 cm^{-1}. Their intensities rose as the molar fraction of $TaCl_5$ increased. A simultaneous decrease of the peaks at 516, 572, 635, 1028, 1223 and 1254 cm^{-1} assigned to Pyr$_{14}$TFMS was also observed.

The SO_3 groups act as electron donors, and the coordination with $TaCl_5$ occurs through the oxygen atom causing the redistribution of the electron density in the SO_3 group. This led to a decrease in the intensity of the vibration δ_s(OSO) at 635 cm^{-1} and appearance of a new peak at 620 cm^{-1}. Simultaneously, the intensity of the vibration $\nu_{as}(SO_2)$ at 1254 cm^{-1} was decreased and a new vibration at 1230 cm^{-1} ap-



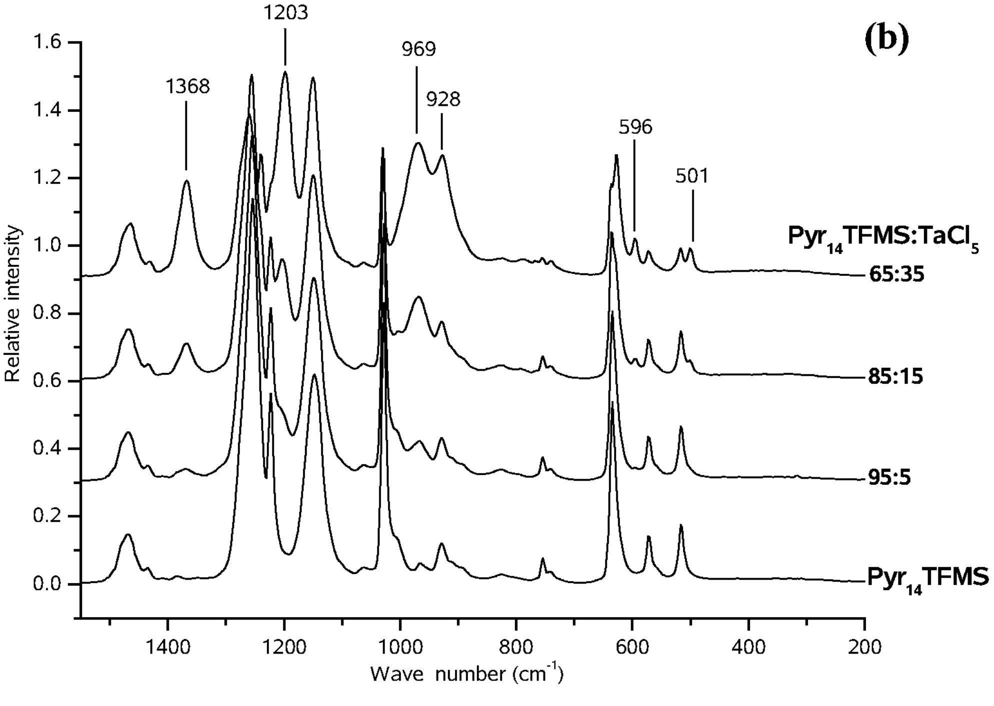


Fig. 3. FTIR spectra of Pyr$_{14}$TFMS-TaCl$_5$ at various molar ratios of components in different ranges: (a) 3400 – 2600 cm^{-1} and (b) 1550 – 200 cm^{-1}.

Complex	Medium	Vibration (cm^{-1})		Reference
$[TaF_6]^-$	Molten alkali fluorides	Ta-F	580 – 607	[22, 23]
	Pyr$_{14}$Cl-K$_2$TaF$_7$	Ta-F	586	[24]
$[TaF_7]^{2-}$	Solid K$_2$TaF$_7$	Ta-F	516 – 542	[25, 26]
	Solid K$_2$TaF$_7$	Ta-F	500 – 505	This work
	Pyr$_{14}$Cl-K$_2$TaF$_7$	Ta-F	516 – 523	[24]
$[TaOCl_4]^-$	CsCl-TaOCl$_3$-TaCl$_5$	Ta=O	960	[27]
$[TaOCl_5]^{2-}$	CsCl-TaOCl$_3$-TaCl$_5$	Ta=O	925	
$[TaOCl_5]^{2-}$	Pyr$_{14}$Cl-TaCl$_5$	Ta=O	928	[28]
$[Ta_2OCl_{10}]^{2-}$	CsCl-TaOCl$_3$-TaCl$_5$	Ta-O-Ta	700 – 870	[27]
$[Ta_2OCl_{10}]^{2-}$	Pyr$_{14}$Cl-TaCl$_5$	Ta-O-Ta	755	[28]
$[TaOF_n]^{(n-3)-}$	LiF-NaF-KF	Ta=O	900	[29]
$[Ta_2OF_{10}]^{2-}$	Organic medium	Ta-O-Ta	880	[30]

Table 2. Vibrational frequencies of fluoro, oxofluoro, and oxochloro species of tantalum(V) formed in different media.

peared as a shoulder as the content of TaCl$_5$ rose. Due to the delocalization of the negative charge in SO$_3$ groups resulting from coordination with TaCl$_5$, the S-O bonds which are not coordinated with tantalum species gained higher energy, resulting in a new vibrational feature observed at 1368 cm^{-1}, whose intensity was increased as the TaCl$_5$ content increased. One can also notice that the vibrations of the Pyr$_{14}^+$ cation at 1469 cm^{-1} [δ (CH$_2$)] and in the range 2880 – 3040 cm^{-1} were unaffected by TaCl$_5$.

New vibrational features observed in the FTIR spectra reflect the interaction of TaCl$_5$ and $[CF_3SO_3]^-$ groups accompanied by the formation of new tantalum(V) species and by structural changes of the $[CF_3SO_3]^-$ groups.

In order to assign the new vibrational features of tantalum(V) species we have summarized the previously reported results on tantalum(V) fluoro, oxofluoro, and oxochloro species formed in different media (Table 2). It was reasonable to assign the new vibration at 596 cm^{-1} to the Ta-F bond formed in hexa-coordinated mixed chloride-fluoride complexes of tantalum(V), $[TaCl_xF_y]^-$ $(x+y=6)$. The vibrations of the $[TaF_6]^-$ anion were observed in molten alkali fluorides at 580 – 607 cm^{-1} [22, 23] and in Pyr$_{14}$Cl at 586 cm^{-1} [24]. The difference in the frequencies of Ta-F vibrations in fluoride (586 cm^{-1}) and mixed chloride-fluoride complexes (596 cm^{-1}) is due to the shorter (and therefore higher energy containing) Ta-F bond in the mixed chloride-fluoride complexes. In hepta-coordinated fluoride complexes of tantalum(V) the Ta-F vibrations were observed at lower frequencies; the spectrum of solid K$_2$TaF$_7$ exhibited the vibrations of [TaF$_7$] units at ~ 500 – 540 cm^{-1} [25, 26, this work] and of Pyr$_{14}$Cl-K$_2$TaF$_7$ at 516 – 523 cm^{-1} [24]. Therefore, we have attributed the vibration at 501 cm^{-1} to Ta-F bond in hepta-coordinated mixed chloride-fluoride complexes, $[TaCl_xF_y]^{2-}$ $(x+y=7)$.

Oxochloride complexes of tantalum(V) were characterized by vibrations at 925 – 928 cm^{-1} and 960 cm^{-1} which are attributed to the stretching of the terminal oxygen in $[TaOCl_5]^{2-}$ and $[TaOCl_4]^-$, respectively [27, 28]. The vibrations at 928 and 969 cm^{-1}, observed in the spectra of Pyr$_{14}$TFMS-TaCl$_5$, were assigned to stretching of the terminal oxygen in the new species $[TaOCl_5]^{2-}$ and $[TaOCl_4]^-$, respectively, which were formed due to the coordination of TaCl$_5$ with $[CF_3SO_3]^-$ groups. At 5 mol% TaCl$_5$ in Pyr$_{14}$TFMS the first species formed were $[TaOCl_4]^-$ anions. At 35 mol% TaCl$_5$ they became the dominant species in the Pyr$_{14}$TFMS-TaCl$_5$ mixture. As the TaCl$_5$ content increased the formation of $[TaOCl_5]^{2-}$ species was observed, but quantitative identification is complicated because of the overlap with the vibration of the pyrrolidinium ring at 929 cm^{-1}.

The vibration at 1203 cm^{-1} in the spectra of Pyr$_{14}$ TFMS-TaCl$_5$ could originate from structural changes of the $[CF_3SO_3]^-$ group due to the interaction with TaCl$_5$.

3.2. Electrochemical Characterization

Cyclic voltammetric measurements were performed in order to estimate the range of electrochemical stability of Pyr$_{14}$TFMS-TaCl$_5$ ionic liquids and to investigate the mechanism of tantalum(V) reduction.

Cyclic voltammograms of pure Pyr$_{14}$TFMS (Fig. 4) showed that the electrochemical stability window of the ionic liquid at 60 °C ranges from about −3.0 V up to approximately 2.0 V. As the temperature increased, the cathodic limit of the applicability of the ionic liquid moved in the anodic direction up to approximately −2.2 V at 170 °C.

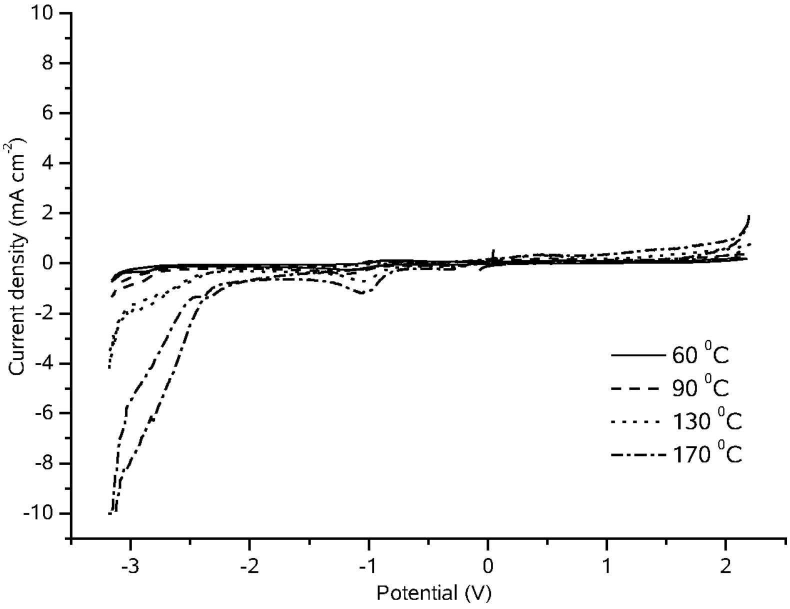


Fig. 4. Cyclic voltammograms of Pyr_{14}TFMS in the temperature range 60 – 170 °C (scan rate 0.1 V s^{-1}).

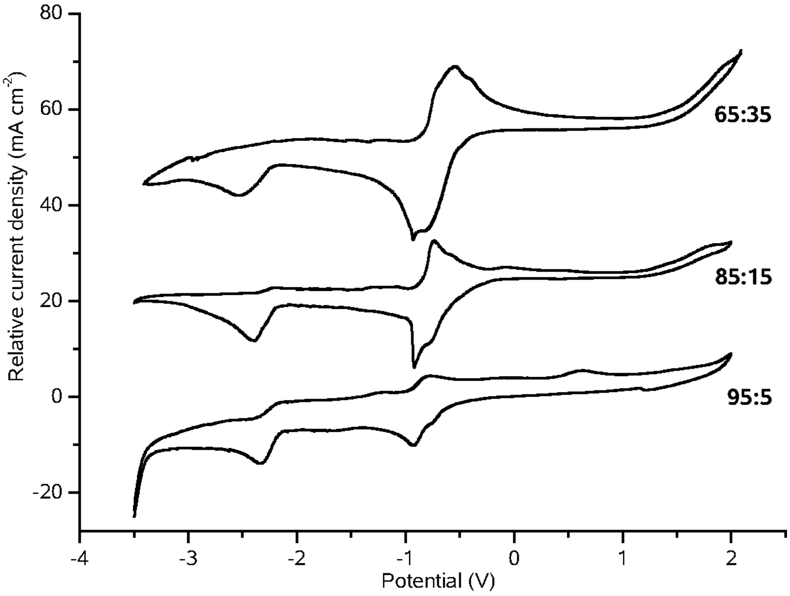


Fig. 5. Cyclic voltammograms of Pyr_{14}TFMS-$TaCl_5$ at various molar ratios of components (80 °C, scan rate 0.1 V s^{-1}).

Cyclic voltammograms of Pyr_{14}TFMS-$TaCl_5$ at molar ratios of 95 : 5, 85 : 15, and 65 : 35 at 80 °C are presented in Figure 5. All three compositions exhibited three reduction peaks: at −0.8 V, −0.9 V, and −2.4 V. The current densities of the first two peaks increased as the molar fraction of $TaCl_5$ in the melt increased, and one can conclude that these peaks are due to reductions of tantalum(V) species. However, as the molar ratio of $TaCl_5$ increased, the current density of the peak at −0.8 V increased faster than the current density of the peak at −0.9 V. According to the FTIR spectra (Fig. 3b) the vibration whose intensity increased significantly as the content of $TaCl_5$ increased from 5 to 35 mol% was attributed to the $[TaOCl_4]^-$ species. Therefore one can correlate the peak at −0.8 V to the reduction of the $[TaOCl_4]^-$ species. The current density of the third reduction peak did not depend on the composition of the melt, remaining constant in all three compositions examined.

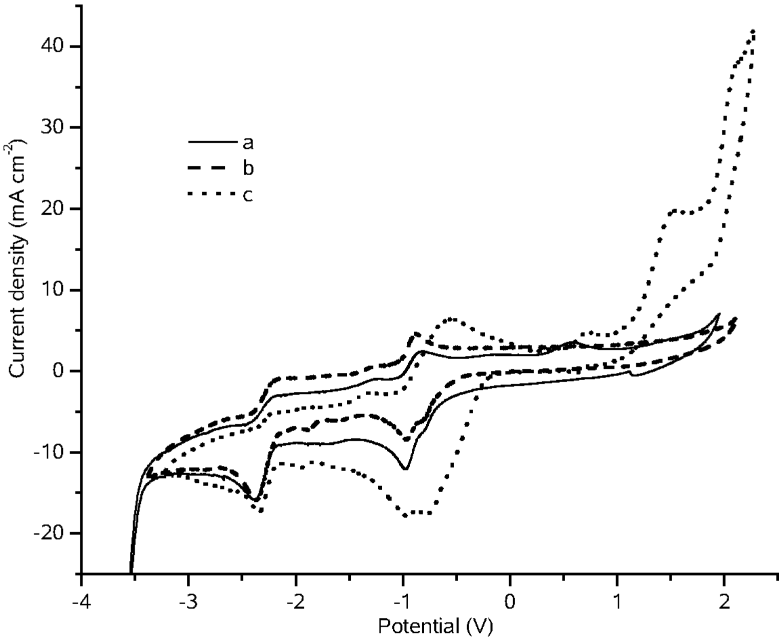


Fig. 6. Influence of oxygen impurities on the electrochemical behaviour of $Pyr_{14}TFMS-TaCl_5$ (95 : 5) (80 °C, scan rate 0.1 V s^{-1}): (a) without oxygen impurities, (b) after a short deliberate inlet of air, and (c) after 72 h.

The influence of oxygen additives (via short inlet of air to the electrochemical cell) on the mechanism of the electrochemical reduction of tantalum(V) species in $Pyr_{14}TFMS-TaCl_5$ was investigated at 80 °C. A cyclic voltammogram of the $Pyr_{14}TFMS-TaCl_5$ (95 : 5) mixture (Fig. 6, curve a) was recorded without oxygen impurities at 80 °C. A cyclic voltammogram (Fig. 6, curve b) was recorded 10 min after a deliberate admission of air to the system, and after 72 h (Fig. 6, curve c). An increase in the current density of the peak at -0.8 V with increasing concentration of oxygen impurities could be observed and it was an additional confirmation that the peak at -0.8 V is due to the reduction of tantalum(V) oxochloride species.

Contradictory views concerning the mechanism of tantalum(V) reduction to tantalum metal in high-temperature molten salts are present in the literature. Some authors suggest a two-step electron transfer [1, 2, 4] while others propose a single-step reduction mechanism [3, 5–7, 13]. In the studies published on electrochemical deposition of tantalum from ionic liquids, two-step reduction mechanisms are proposed [10, 11].

We suggest that the first reduction peak at -0.8 V corresponds to the reduction of $[TaOCl_4]^-$ complexes of tantalum(V) to tantalum oxides. The second reduction wave at -0.9 V may be due to the first reduction step of the mixed chloride-fluoride species of tantalum(V), whose formation was confirmed by FTIR spectroscopic data:

$$[TaCl_xF_y]^- + e^- \rightarrow [TaCl_xF_y]^{2-}.$$

The third reduction peak at -2.4 V could be attributed to further reduction of tantalum.

According to the data obtained, the reduction of tantalum(V) oxochloride species occurs before the first reduction step of the mixed chloride-fluoride complexes of tantalum. Therefore, the codeposition of tantalum oxides cannot be avoided during the electrochemical deposition of tantalum from this system.

The mechanism of tantalum(V) reduction in the $Pyr_{14}TFMS-TaCl_5$ ionic liquid is very complicated due to the coexistence of different species, such as: $[TaOCl_4]^-$, $[TaOCl_5]^{2-}$, $[TaCl_xF_y]^-$ $(x+y=6)$, $[TaCl_xF_y]^{2-}$ $(x+y=7)$, and $[TaOCl_xF_y]^{z-}$.

4. Conclusions

The formation of mixed oxochloride and chloride-fluoride complexes of tantalum(V) in the ionic liquid $Pyr_{14}TFMS-TaCl_5$ with 5, 15, and 35 mol% $TaCl_5$ was confirmed by means of FTIR spectroscopy. The increase of the content of $TaCl_5$ was accompanied by an increase in the content of oxochloride complexes, primarily $[TaOCl_4]^-$ which is the dominant species in these ionic liquids.

Electrochemical measurements were in agreement with spectroscopic data. The cyclic voltammograms exhibited an increase in the current density of the first reduction peak at -0.8 V, attributed to the reduction of $[TaOCl_4]^-$ complexes, as the content of $TaCl_5$ increased in the ionic liquids.

The formation of oxochloride complexes could be a restricting factor in the electrochemical deposition of tantalum from Pyr_{14}TFMS-$TaCl_5$ ionic liquid.

Acknowledgement

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