

Spectroscopy of Refractory Metals in Ionic Liquids and its Application to the Understanding of the Mechanism of Electrochemical Reduction

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Coordination chemistry of refractory metals in ionic liquids is completely unknown. FTIR-, *in situ* FTIR-emission and Raman spectroscopic studies were performed in order to obtain the information about the structure and composition of niobium (V), tantalum (V), and titanium (IV) species in pyrrolidinium and imidazolium based ionic liquids and the nature of their interaction with the functional groups of organic components.

A variety of the novel pyrrolidinium and imidazolium based ionic liquids with the salts of refractory metals in respect to their electrochemical application were obtained by combining of organic component with the salts of refractory metals at various molar ratios of the components.

Inorganic components used: TaCl₅, TaF₅, K₂TaF₇, NbCl₅, NbF₅, K₂NbF₇, TiF₄.

Organic components consist of:

- 1-butyl-1-methylpyrrolidinium chloride (Pyr₁₄Cl)
- 1-hexyl-1-methylpyrrolidinium chloride (Pyr₁₆Cl)
- 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (Pyr₁₄ TFMS)
- 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (Pyr₁₄ TFMSI)
- 1-butyl-1-methylpyrrolidinium tetrafluoroborate (Pyr₁₄BF₄)
- 1-propyl-1-methylpyrrolidinium tetrafluoroborate (Pyr₁₃BF₄)
- 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄)
- 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (BMMImBF₄)

Four different groups of ionic liquids were obtained and investigated:

- chloride mixtures: (x)Pyr₁₄Cl-(1-x)TaCl₅, (x)Pyr₁₄Cl-(1-x)NbCl₅, (x)Pyr₁₆Cl-(1-x)TaCl₅ (x=0.90-0.20);
- chloride-fluoride mixtures: (x)Pyr₁₄Cl-(1-x)K₂TaF₇, (x)Pyr₁₄Cl-(1-x)K₂NbF₇ (x=0.90-0.30) ;
- fluoride mixtures: (x)BMMImBF₄-(1-x)TiF₄ (x=0.98-0.65), BMImBF₄-NbF₅, Pyr₁₄BF₄-TaF₅ ;
- oxygen-containing chloride-fluoride mixtures: (x)Pyr₁₄TFMS-(1-x)TaCl₅ (x=0.95-0.65), (x)Pyr₁₄TFMSI-(1-x)TaCl₅ (x=0.95-0.30) etc.

Ionic liquids on the base of Pyr₁₄Cl (simple Cl-anion).

Raman spectroscopy was used to investigate the complex formation of tantalum(V) in the mixtures of (x)Pyr₁₄Cl-(1-x)TaCl₅ (x=0.80-0.30) over the temperature range 20-160°C. Depending on the molar composition, different species of tantalum (V) were identified. In the *basic* and *neutral* mixtures of (x)Pyr₁₄Cl-(1-x)TaCl₅ (x=0.80-0.50), tantalum(V) exists in the form of octahedral [TaCl₆]⁻ in both solid and molten states. In *acidic* ionic liquids (x=0.45-0.30) [Ta₂Cl₁₀]²⁺ units are the main species of tantalum(V) identified in the solid state. As the temperature rose, the gradual degradation of [Ta₂Cl₁₀]²⁺ units was observed in the solid state accompanied by the formation of [TaCl₆]⁻ and [Ta₂Cl₁₁]⁻ anions. In the molten state, in the range between 130°C and 160°C the latter two

species exist in equilibrium and are the dominant species of tantalum(V) /1, 2/.

In the mixtures (x)Pyr₁₄Cl-(1-x)NbCl₅ (x=0.90-0.30) the formation of the niobium(V) and niobium (IV) species was observed in basic ionic liquids.

In the mixtures (x)Pyr₁₄Cl-(1-x)K₂TaF₇ the equilibrium [TaF₇]²⁻ ↔ [TaF₆]⁻ was established. This equilibrium shifts toward [TaF₇]²⁻ as the mole fraction of K₂TaF₇ increases and it shifts toward the [TaF₆]⁻-complexes when passing from LiF to CsF additives.

Ionic liquids with the complex anion of the organic component (BF₄⁻, CF₃SO₃⁻). In fluoride mixtures (x)BMMImBF₄-(1-x)TiF₄ (x=0.98-0.65) the analysis of the spectra allow identify the presence of TiF₄ and TiF₆²⁻ complexes in the system. As the concentration of TiF₄ increases, the interaction of TiF₄ with BF₄⁻ group leads to the formation of hetero-nuclear complexes TiBF₈⁻ that shared a common edge. The reactions 2BF₄⁻ + TiF₄ → TiF₆²⁻ + 2BF₃↑ and BF₄⁻ + TiF₄ → TiBF₈⁻ take place in ionic liquid and they are intensified as the concentration of TiF₄ in ionic liquid increases and the temperature rises up /3/.

In ionic liquids Pyr₁₄TFMS-TaCl₅ initially containing oxygen in the functional group [CF₃SO₃]⁻, the formation of oxohalide complexes of tantalum(V) was confirmed by spectroscopic methods /4/.

The peculiarities of the formation of oxohalide complexes of tantalum(V), niobium(V) and titanium(IV) in ionic liquids were investigated as their formation is a crucial factor in successful electrochemical deposition of refractory metals. The formation of oxohalide complexes of tantalum(V) in ionic liquids Pyr₁₄Cl-TaCl₅ and Pyr₁₄Cl-K₂TaF₇ with the additives of Na₂O (at various ratios n_O/n_{Ta}) was estimated by means of FTIR- and Raman spectroscopy. The formation of oxochloride complexes could be a restricting factor in the electrochemical deposition of tantalum from Pyr₁₄TFMS-TaCl₅ ionic liquid and from other ionic liquids under the conditions where the formation of oxohalides complexes takes place.

Spectroscopic data obtained were used for the identification of the electrochemical active species of tantalum(V), niobium(V), and titanium(IV) in ionic liquids and the understanding of the mechanism of their electrochemical reduction /3,4,5/. These and other spectroscopic and electrochemical data obtained for tantalum(V), niobium(V), and titanium(IV) species in ionic liquids listed above will be summed in this presentation.

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