

Electrochemical reduction of TiCl_4 in Imidazolium based ILs with Azide and Tetrafluoroborate anions

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Since the discovery of the new class of substances with low melting points, named ionic liquids (ILs), the electrochemistry of refractory metals in these electrolytes was widely investigated.

Trialkylsubstituted imidazolium cation-based ILs offer sufficient cathodic stability, due to the substitution of the weakly acidic proton, compared to dialkylated ILs. The anodic stability of ILs with tetrafluoroborate anion is about 1.5V higher than of ILs which have an azide anion. The cathodic stability exhibits the same behaviour.

1-butyl-2,3-dimethyl imidazolium azide (BMMImN_3) is a potentially environmentally friendlier electrolyte, but due to the formation of the strong azide complexes, Ti(IV) reduction to metallic titanium is complicated.

Electrochemical behaviour of TiCl_4 was studied in BMMImN_3 and BMMImBF_4 ILs at 65°C . Ti(IV) electroreduction mechanism was investigated with chronopotentiometry (CP) and cyclic voltammetry (CV) methods in melts with different concentrations of TiCl_4 . According to FTIR investigations, Ti(IV) in BMMImN_3 exists in form of a hexaazidotitanate complex which reduction is limited to a one electron step. In BMMImBF_4 , a consecutive four-electron reduction is observed. Diffusion coefficients

of Ti(IV) in these ILs at temperature 65°C were calculated based on the CP measurements (Fig.1):

in BMMImN_3 –

$$D_{\text{Ti(IV)}} = (1.3 \pm 0.6) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1};$$

in BMMImBF_4 –

$$D_{\text{Ti(IV)}} = (2.04 \pm 0.1) \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}.$$

The mechanism of Ti(IV) reduction will be discussed.

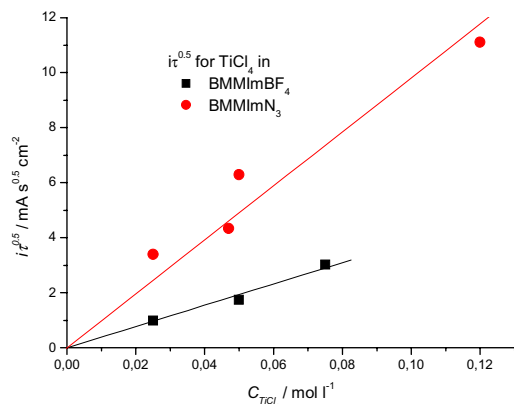


Fig.1. Analysis of transition times for the first reduction step ($\text{Ti(IV)} \rightarrow \text{Ti(III)}$).

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