

Dependence of the Electrochemical Windows in Ionic Liquids on Water Content

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Room temperature ionic liquids (RTIL) are organic salts which are liquid at or near room temperature. They are promising candidates for many applications due to low to non-volatility, high intrinsic conductivity, thermal and chemical stability and a large electrochemical window (ECW) up to 7 V. Their properties can be tuned by changing the cation and anions offering vast possibilities. Therefore, they were, for example, suggested as electrolytes for oxygen electrocatalysis in metal air batteries¹ and electrocatalysis of CO₂². However, the accessible electrochemical window is sensitive to impurities from the synthesis or more importantly to water uptake from air. RTILs can be either hydrophobic or hydrophilic depending on the selected cation and anion. However, both tend to take up water from the environment³ leading to a decrease in the electrochemical window. There are studies investigating the effect of humidity on the electrochemical window of some RTILs^{3,4}. However, systematic studies on the effect of the addition of water on the anodic and cathodic limit for imidazolium-based RTILs are still rare. Therefore, we investigated the limits for 1-Butyl-3-methylimidazolium triflate [BMIM][OTf] while systematically adding milli-Q water in a range from 0.66 % v/v (0.08 N_{H_2O}/N_{IL} fraction) to 60 % v/v (20 N_{H_2O}/N_{IL} fraction) on both platinum and gold electrodes. The triflate [OTf] anion was selected, because it was reported to be resistant to hydrolysis⁵ while having a ECW of ~4.5 V and being miscible with water. The experiments were carried out in a 3-electrode setup using a curled platinum wire as counter electrode, a leakless Ag/AgCl, and Pt or Au wires with fixed area (PTFE heat shrink tube). We found that the ECW at lower water contents is nearly independent of the electrode material, however for higher water content the ECW differs significantly (~0.5V) between Pt and Au (Figure 1), mainly due to the different behavior of the cathodic limit. This may be explained due to the better catalytic HER property of Pt. Surprisingly, even at higher water contents of 60 % v/v (20 N_{H_2O}/N_{IL} equivalent to ~ 2.71 M IL in H₂O) the EC window was still 2.4 V (Pt) and 2.9 V (Au) and seem to stabilize at these values.

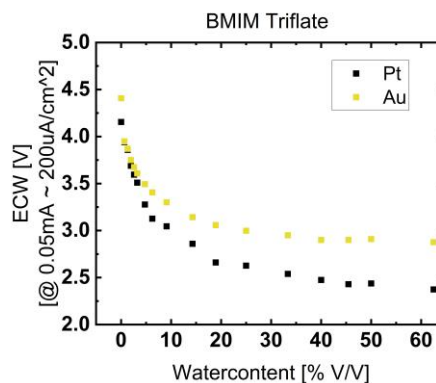


Figure 1: Electrochemical window of [BMIM][OTf] with increasing water content on platinum and gold electrodes at a current of 0.05 mA (~200 $\mu\text{A}/\text{cm}^2$) in the cathodic (anodic limit) and anodic (cathodic limit) scan direction.

References:

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