

The effect of water addition on Zn/Zn(II) redox reactions in bis(trifluoromethanesulfonyl)imide based room temperature ionic liquids

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Recently, with the need for high stability against moisture and low solubility for water, hydrophobic room temperature ionic liquids (RTILs) have qualified as fascinating electrolytes in the field of energy storage devices, such as batteries (1), supercapacitors (2) and fuel cells (3). Particularly, hydrophobicity is considered as a desirable property for electrolyte candidates used in metal-air batteries, which need air but not moisture (4), since moisture absorption reduces the electrochemical window, i.e., the electrochemical stability of RTILs. Nevertheless, it has been pointed out that the so called "hydrophobic" RTILs can still absorb considerable amounts of water (up to 1.0 wt% H<sub>2</sub>O) from the atmosphere over time (5). A positive effect is that water can serve as a diluent for reducing the relatively high viscosity of RTILs and improving the conductivity. Therefore, it would be of particular importance, in view of both theoretical and practical aspects, to explore the effect of water on RTILs.

It is of interest to study the effect of water addition on the electrochemical properties of Zn redox, including reversibility and kinetic properties. Among the hydrophobic RTILs, those composed of bis(trifluoromethanesulfonyl)imide ([TFSI]<sup>-</sup>) anions have received great interest as the electrolyte component for energy-storage devices, especially in state-of-art Li ion batteries (6-8). In this study, three RTILs based on [TFSI]<sup>-</sup> anions, i.e., 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI), 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MP3P-TFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI), were selected. The variation in Zn redox behavior with the addition of water was investigated, with the aim of revealing the mechanism associated with water absorption as well the optimal amount of water that can be added as diluent.

Preliminary results for the BMP-TFSI system show that with water additions in excess of 2.0 wt%, Zn/Zn(II) redox occurs at a similar potential as for decomposition of the bulk ionic liquid, which is indicated by the continuous drop in current density on the reduction side (Figure 1 (a)). It is, therefore, not reasonable and practical to add H<sub>2</sub>O exceeding 2.0 wt%. Complete Zn/Zn(II) redox reactions are observed when the water content is ≤ 2.0 wt% (Figure 1 (b)). Moreover, the reversibility of Zn/Zn(II) redox is enhanced with water addition, as revealed by the reduced peak potential separation between Zn/Zn(II) oxidation and reduction,  $\Delta E_p$ . For Zn/Zn(II) redox in blank BMP-TFSI,  $\Delta E_p$  is close to 0.9 V, but  $\Delta E_p$  drops significantly to less than 0.6 V after adding up to 2.0 wt% water (regardless of the water amount). In addition, compared with blank BMP-TFSI, both the diffusion coefficient for the Zn species and

the exchange current density for Zn/Zn(II) redox reactions increase by approximately 70% in BMP-TFSI with 2.0 wt% water addition (figures not shown).

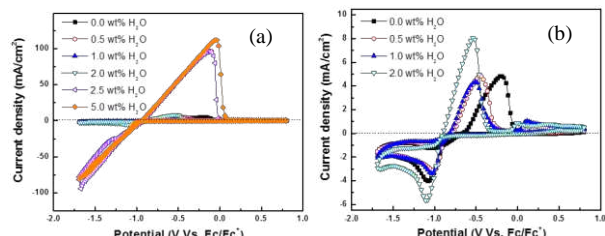


Figure 1 CV comparisons (scan rate of 100 mV/s) for Zn/Zn(II) redox reactions in BMP-TFSI with different water additions: (a) 0.0-5.0 wt% and (b) 0.0-2.0 wt%.

Similar studies for Zn redox in MP3P-TFSI and EMI-TFSI (Figure 2) show that the addition of 2.0 wt% H<sub>2</sub>O can also decrease the  $\Delta E_p$ . In particular, for EMI-TFSI (Figure 2b) an obvious improvement in Zn redox reversibility is observed ( $\Delta E_p$  decreases by more than 60%). However, in MP3P-TFSI (Figure 2a), after adding 2.0 wt% water, the Zn oxidation process is suppressed, indicating the irreversibility of the Zn redox reaction. The optimal amount of water addition in these two RTILs is still under investigation.

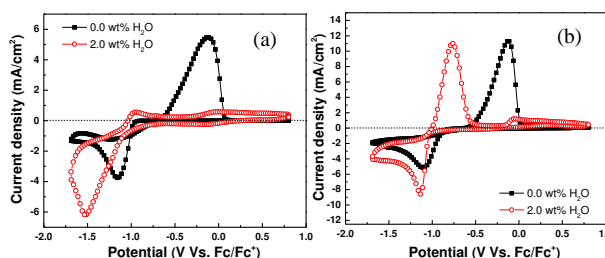


Figure 2 CV comparisons (scan rate of 100 mV/s) for Zn/Zn(II) redox reactions with water additions between 0.0 wt% and 2.0 wt%: (a) MP3P-TFSI and (b) EMI-TFSI.

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