



Stable zinc cycling in novel alkoxy-ammonium based ionic liquid electrolytes



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ABSTRACT

High-energy density Zinc-air batteries are currently of interest since they could play a key role in emerging large-scale energy storage applications. However, achieving good rechargeability of such metal-air batteries requires significant further research and development effort. Room Temperature Ionic liquids (RTILs) offer a number of ideal thermal and physical properties as potential electrolytes for large-scale energy storage applications and thus, can help increase the practicality of such electrochemical devices. This paper reports the synthesis and application of three novel quaternary alkoxy ammonium bis (trifluoromethylsulfonyl)amide based RTILs, with two or more ether functional groups designed to interact and solubilize zinc ions, in order to aid in the electrochemical reversibility of the metal. The anion is successfully reduced from, and re-oxidized into, the three alkoxy ammonium RTILs suggesting that they are potential candidates as electrolytes for use in zinc-air batteries. Cyclic voltammetry reveals that the presence of water reduces the activation barrier required to deposit zinc and assists stable charge/discharge cycling in an electrolyte consisting of 0.1 M Zn(NTf₂)₂ in the tri-alkoxy ammonium chain RTIL, [N₂(20201)(20201)(20201)] [NTf₂], with 2.5 wt.% H₂O. Further experiments demonstrate that with such electrolyte a Zn electrode can complete at least 750 cycles at a current density of 0.1 mA/cm² at room temperature.

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1. Introduction

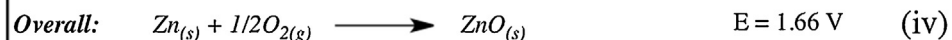
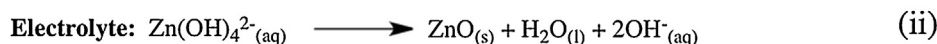
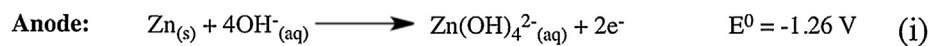
Room temperature ionic liquids (RTILs) [1–10] have attracted great attention as potential electrolytes in the development of advanced battery technologies. Their characteristic properties of high conductivity, low volatility and low flammability would be ideal for reversible zinc-air batteries, where currently the aqueous alkaline conditions of the electrolyte are responsible for many of the failure mechanisms of the primary device. Zinc-air batteries consist of a zinc anode with the cathode reducing oxygen. The electrochemical reactions occurring in this battery are shown in Scheme 1 [11–15]. When the battery is discharged in the presence of an alkaline electrolyte, zinc hydroxide is produced, which is

converted into insoluble zinc oxide (ZnO) when the solubility limit of the hydroxide species is reached. The formation of solid ZnO can be a difficult process to reverse during recharge, as it relies on the resolubilization of the Zn species back into the electrolyte prior to reduction [16]. In addition, CO₂, which also enters from the atmosphere through the pores of the cathode, reacts with the aqueous electrolyte to form insoluble bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) salts, blocking the electrode-electrolyte interface and preventing long-term cycling of the battery [17].

Recent literature has demonstrated that the electrochemical deposition of zinc from various RTILs is possible and offers advantages over organic and aqueous electrolytes, which suffer from issues such as volatility, instability and flammability [18–27]. RTILs can help overcome the above limitations of zinc electrochemistry in a number of ways. Firstly, in the context of a Zn-air cell, the use of the non-volatile RTIL instead of the aqueous electrolyte eliminates the possibility of evaporation, preventing

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Scheme 1. Main chemical reactions occurring in a primary zinc-air cell under alkaline conditions reproduced from Kar, M., Simons, T.J., Forsyth, M. and MacFarlane D. R., *PCCP*, 2014, **16**, 18658–18674.

the cell from “drying out” [23]. Secondly, the structural properties (i.e. molecular interactions of the cations and anions) of RTILs are tuneable, whereby attaching certain functional groups can enhance coordination to the zinc ions in the electrolyte and hence avoid formation of oxide/hydroxides or other undesirable by-products. Manipulation of the donor atom/ Zn^{2+} interactions has been shown to play a large role in determining whether Zn reduction produces a smooth, non-dendritic morphology [22]. This concept is well known and exploited in the traditional electroplating industry by the addition of organic and inorganic compounds (known as “brighteners”) to electroplating baths [28,29]. The addition of solvents or additives can also enhance the mobility of zinc ions in an RTIL, resulting in higher ionic conductivity (and hence Zn deposition and stripping currents). Currently, the electrochemical performance of a rechargeable zinc-air battery in RTILs is being studied by a number of research groups [22,23,28–31]. However, this work is still very much in progress.

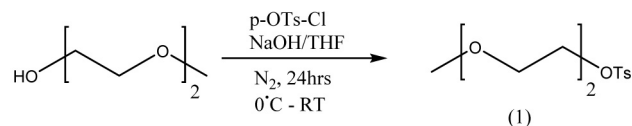
It is commonly known that due to their Lewis basicity, the oxygen atoms in ethereal solvents such as tetraglyme, $\text{CH}_3\text{O}(-\text{CH}_2\text{CH}_2\text{O}-)_4\text{CH}_3$, are able to strongly bind to Lewis acids such as Li^+ and Zn^{2+} ions [32–36]. Recent advances have shown that incorporating such ethereal functional groups into the cation can improve the physical and electrochemical properties of RTILs [37–40]. In our previous work on designing novel electrolytes for zinc-air batteries, the inclusion of various oligo-ether side chains into a quaternary ammonium cation, with bis (trifluoromethylsulfonyl) imide $[\text{NTf}_2]^-$ as the anion, was found to enhance the coordination and solubility of zinc ions and enhance the deposition and stripping reactions [40]. It was demonstrated that while quaternary cations with one long oligo-ether chain-length produced a lower viscosity than the shorter chain side groups, zinc electrochemistry was better facilitated in the latter RTIL. This suggests that, upon the addition of zinc, the RTIL with the longer ether chain complexes more strongly to the metal ion, increasing the overall viscosity and decreasing the ability of the Zn^{2+} ions to be easily reduced. Therefore to maintain a similar low viscosity, while also further increasing the mobility of the Zn^{2+} ions to better facilitate their electrochemistry, a related, novel family of quaternary ammonium RTIL cations with multiple oligo-ether based functionalised groups, such as the di-alkoxy $[\text{N}_{22(20201)(20201)}]^+$ and the tri-alkoxy $[\text{N}_{2(20201)(20201)(20201)}]^+$, in addition to the mono-alkoxy $[\text{N}_{222(20201)}]^+$ cation (See Scheme 1), were synthesized and studied in this current work. It is hypothesized that the use of multiple ether-based functional groups can eliminate the formation of any complex “crown ether like” cyclic structure that can arise from the use of a long oligo-ether type chains, and thus support the electrochemical reversibility of zinc [24]. The electrochemical behavior and long-term charge/discharge cycling of zinc in the

three RTIL/Zn mixtures (Scheme 2) are also studied here. Given water will be present in a zinc-air battery from moisture, and is likely to improve the transport properties of the electrolyte, RTIL/Zn mixtures with added water were included in the studies.

2. Experimental

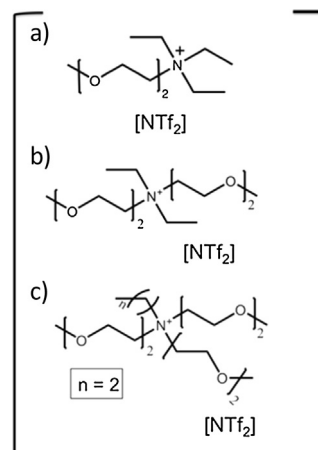
The synthesis of N,N,N-triethyl-2-(2-methoxyethoxy) ethanyl-ammonium bis(trifluoromethylsulfonyl) imide $[\text{N}_{222(20201)}] [\text{NTf}_2]$, N,N-diethyl-2-(2-methoxyethoxy)-N-(2-(2-methoxyethoxy) ethyl) ethan-1-aminium bis(trifluoromethylsulfonyl) imide $[\text{N}_{22(20201)(20201)}] [\text{NTf}_2]$ and N-ethyl-2-(2-methoxyethoxy)-N,N-bis(2-(2-methoxyethoxy) ethyl) ethan-1-aminium bis(trifluoromethylsulfonyl) imide, $[\text{N}_{2(20201)(20201)(20201)}] [\text{NTf}_2]$ are described below:

a)



2.1. Synthesis of 2-(2-methoxyethoxy)ethyl 4-methylbenzene sulfonate (1)

Sodium hydroxide (20 g, 0.5 moles) in water (20 ml) was added to diethyl glycol monomethyl ether (40 g, 0.33 moles) in THF (60 ml) and the solution was cooled to 0 °C. *p*-Tosyl chloride



Scheme 2. Schematic of a) $[\text{N}_{222(20201)}]^+$, b) $[\text{N}_{22(20201)(20201)}]^+$ and c) $[\text{N}_{2(20201)(20201)(20201)}]^+$ $[\text{NTf}_2]^-$ based RTILs.

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