Activity and Stability of Bifunctional GDE in Ionic Liquid for Zn–Air Battery

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Introduction

Because of their higher theoretical energy density, lower toxicity, less expensive electrode materials and non-affinity to thermal runaway like e.g. Li-based systems, metal/air battery such as Zn/air is potential candidates for sustainable energy storage applications. However, large scale commercialisation is hindered by some inherent drawbacks related to the metal electrode such as poor reversibility, shape change and dendrite formation as well as low energy efficiency due to high overpotential and carbonate precipitation at the air electrode in alkaline electrolyte. In this context, recent developments in ionic liquids (IL) based protic electrolyte such as DEMA TfO + Zn TfO open exciting perspectives especially with respect to suppression of carbonate formation and evaporation of electrolyte.

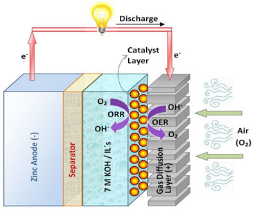


Fig. 1: Working principle of a rechargeable Zn/air battery in KOH

ORR in ionic liquids

Room Temperature Ionic liquids (RTILs) are low temperature (<100°C) molten salts composed of organic cations and anions characterized by extremely low vapor pressure, high decomposition temperature, but also by high viscosity and poor/moderate conductivity. For electrochemical applications, and more especially for metal/air battery in which oxygen reactions occur, presence of proton species in ionic liquid is preferred since aprotic ones allow "only" 1e⁻ oxygen reduction reaction (ORR) step. By adding 0.1 M triflic acid (Tf) to BdMim, Friesen coworkers yielded a 3.5 e⁻ step during ORR at Pt. However, presence of water may be a concern for electrolyte stability.

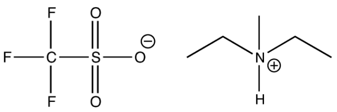


Fig. 2: Structure of DEMA TfO

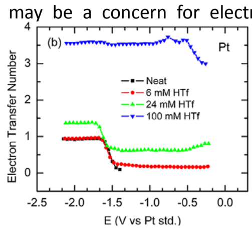


Fig. 3: Electron transfer number plots during ORR at Pt with increasing concentration of protic species

Oxygen reduction reaction in aprotic ionic liquid proceeds by quasi reversible reduction of oxygen to form a superoxide radical. In presence of protic species the 1 e⁻ quasi reversible reduction step will be followed by protonation of superoxide to form hydroperoxyl radical and then peroxide. Presence of Pt site promotes the reduction to water.

$$O_2 \xleftrightarrow{e^-} O_2^{\bullet-} \xleftrightarrow{H^+} HO_2^{\bullet-} \xleftrightarrow{e^-+H^+} H_2O_2 \xleftrightarrow{2e^-+2H^+} H_2O$$

Aprotic IL — Protic IL — Protic IL at Pt

Fig. 4: ORR/OER reactions in ionic liquids

E. Switzer, R. Zeller, Q. Chen, K. Sieradzki, D. Buttry, C. Friesen, J. Phys. Chem. C. 117 (2013) 8683–8690
M. Kar, T. Simons, M. Forsyth, D. MacFarlane, Phys.Chem.Chem.Phys. 16 (2014) 18658 -18674.

EL-Cell assembly and half cell measurements

- Working Electrode (WE) and Counter Electrode (CE) are separated by a fiber glass separator (1.55 mm thick) filled with electrolyte (300 µL)
- High precision 18 mm diameter sandwich geometry for the electrodes accommodates a CE (Zn metal foil) on bottom, WE (air cathode) on top and Reference Electrode (RE) of Zn/Pt wire (∅: 1 mm, L: 4 mm) within the separator
- Pt/C : 1 mg_{Pt} cm^{-2} of 20 wt% Pt/Vulcan carbon XC-72 (Quintech: EC-20-10-7)
- Zn Foil : 99.99% pure / 0.1 mm thick (Chempur: 009524)

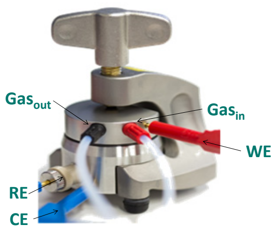


Fig. 5: EL-Cell set up

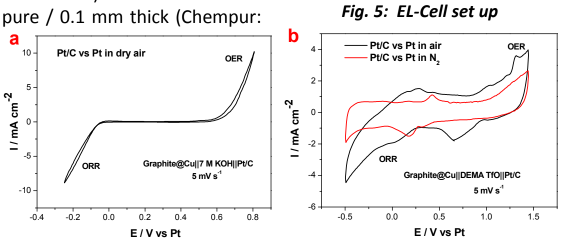


Fig. 6: CV of Pt/C GDE in a) 7 M KOH & b) DEMA TfO + 0.01 M Zn TfO at 22°C

- Bifunctional activity of Pt/C GDE was studied by cyclic voltammetry in half cell condition
- ΔE for bifunctional activity of Pt/C has increased from 800 mV (7 M KOH) to 1500 mV (DEMA TfO) at 3 mA cm^{-2}

Reversible zinc deposition in DEMA TfO

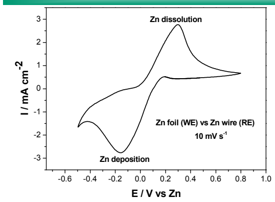


Fig. 6: CV of DEMA TfO + 0.01 M Zn TfO at 22°C in air

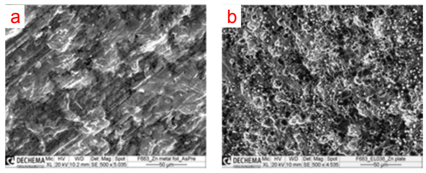


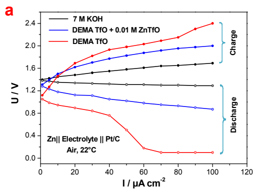
Fig. 7: SEM of (a) pristine Zn plate & (b) Zn foil after three days of operation in DEMA TfO + 0.01 M ZnTfO

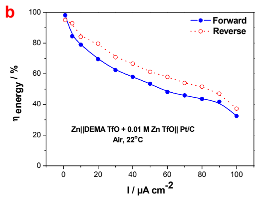
- Zinc deposition/dissolution was studied by cyclic voltammetry in half cell condition
- Quasi reversible process was observed on CV
- Zn island-like structure can be seen on SEM while dendrite formation is inhibited

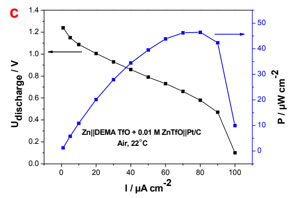
Full cell measurements

- Full cell measurements were carried out in EL-cell assembly with Pt/C GDE. The U-I characteristics were obtained by charging-discharging the cell for 15, 60 and 120 min respectively.

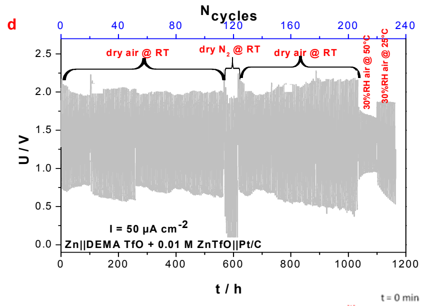
Fig. 8: Full cell measurements in DEMA TfO + Zn TfO
(a) U-I characteristics in different electrolytes
(b) Relationship between energy efficiency and current density
(c) Power density curve of ORR at Pt/C
(d) Cycling of Zn/air battery in 5 h cycles: 2 h charge/discharge steps and 1 h at OCV
(e) Evaluation of cell capacity at 10 µA cm⁻² in function of temperature

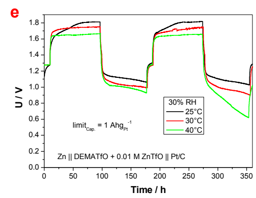






- Addition of zinc salt to ionic liquid is necessary to lower potential gap between charge and discharge
- At 50 µA cm^{-2}, cell power density amounts about 40 µW cm^{-2}
- Excellent stability of Zn/air cell with IL in dried and humidified air @ 50 µAcm^{-2} for 1100 h.





- CA of DEMA TfO on Pt/C GDE surface < 110°C: no TPB formation → electrode flooding!

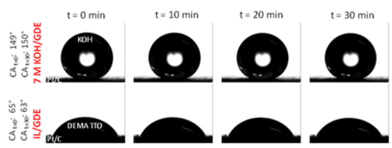


Fig. 9: Contact angle (CA) measurement of 7 M KOH and DEMA TfO on Pt/C GDE

Conclusions

- Feasibility and reversibility of Zn||DEMA TfO + Zn TfO||Pt/C has been demonstrated for the first time.
- Use of DEMA TfO has enabled to overcome several inherent challenges of KOH systems:
  - ✓ **Reversible Zn deposition without dendrite formation**
  - ✓ **Comparable energy efficiency for oxygen reactions (≈60% @ 50 µAcm^{-2})**
  - ✓ **Higher cycling stability (>1100 hours)**
  - × ***However, current density is 25 times lower in IL compared to KOH due to absence of TPB!***

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