

Test of different aprotic ionic liquids for the Al/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 batteries such as Al-Air (8040 vs. 2046 AhL-1 for Li) are potential candidates for sustainable energy storage applications. Average capacity and energy values of most common metal/air systems from references [1-4] are listed below. Because of its low cost and abundance Al is an interesting candidate for this type of battery. However, large scale commercialization is hindered by some inherent drawbacks related to the metal electrode such as irreversibility (not electrochemically rechargeable), passivation and parasitic hydrogen evolution as well as low energy efficiency (1). In this context, recent developments in aprotic room temperature ionic liquids (RTIL) based electrolytes such as 1-Ethyl-3-methylimidazolium chloride and 1-Butyl-1-methyl-pyrrolidinium (BMPyr) chloride + aluminum chloride open new perspectives for Al deposition/dissolution, especially with respect to suppression of passive layer formation and self-discharge due to hydrogen evolution (2,3). Most of the ILs, however, are highly viscous and consequently have a low ionic conductivity that drastically limits reaction kinetics. Other crucial aspects are related to the low surface tension of pure ILs compared to water that commonly hinders triple phase boundary (TPB) formation at the gas diffusion electrode (GDE).

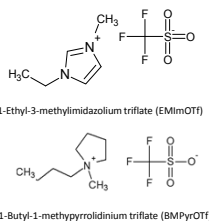


Fig. 1: Chemical structures of EMImOTf and BMPyrOTf

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		Al	Li	Si	Zn
Theoretical voltage	V	2.7	3.4	~ 3	1.6
OCV	V	1.5 ^a	2.9 ^b	1.4 ^a	1.6 ^a
Voltage @ I nominal	V	1.1-1.4	2.4	0.8-1.0	1.0-1.1
Capacity per mass*	Ah/g	3	3,8	3.8	0.8
Capacity per volume*	Ah/cm ³	8.0	2,1	8.8	5.8
Specific energy	Wh/kg	8146	11246	8470	1363
Energy density	Wh/l	21994	5960	19800	9677

Objectives & backgrounds

The "AlSiBat" project aims at the development of a primary Si/air and secondary Al/air battery with appropriated IL-based electrolytes. The R&D activities in DFI focus on the development of bifunctional catalysts and GDEs for IL-based Al/air cell. Most important challenge consist on finding a stable electrolyte suitable for ORR/OER, triple phase boundary formation and Al deposition/dissolution.

- ORR in ILs leads to reversible formation of superoxide ion, stabilized by IL cation:
 $O_2 + e^- \rightleftharpoons O_2^-$
- In protic ILs this can be reduced further to hydrogen peroxide. At Pt electrodes, water can be formed [5-7].
- In acidic EMImCl/AlCl₃ melts, dominant species is Al₂Cl₇⁻. Al electrodeposition process in acidic melts take place following reversible reaction [8]:
 $4Al_2Cl_7^- + 3e^- \rightleftharpoons Al + 7AlCl_4^-$

Contact angle measurements

- Contact angles of some preselected aprotic ionic liquids such as EMImOTf, EMImOAc and BMPyrOTf were screened with respect to their contact angle on Pt/C and LCCO/C gas diffusion electrodes in function of time (see Fig. 2).

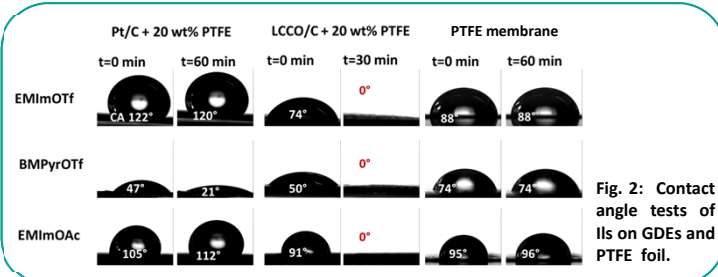


Fig. 2: Contact angle tests of ILs on GDEs and PTFE foil.

- On Pt/C GDE, a stable droplet formation with contact angle (CA) > 110° was only observed for EMImOTf and EMImOAc.
- After 12 hours, EMImOTf was flooding the GDE. EMImOAc is highly hygroscopic.
- On PTFE foil, all ILs formed a stable droplet. Max. CA only 95° with EMImOAc.
- It appears that contact angle value is not only depending on liquid surface tension but also on that of the substrate; TPB cannot be formed on LCCO/C electrode [9].

OER/ORR in pure IL electrolyte

Cyclic voltammograms (CV) on activity of Pt/C for OER/ORR were performed in pure ILs and with Pt as counter and reference electrode. Activity and onset potential for OER and ORR can be deduced from the difference in charge and peak shape air and N₂.

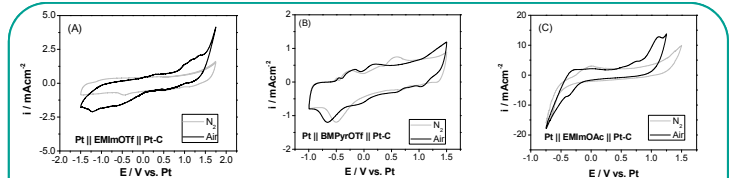


Fig. 3: CVs of Pt/C in (A) EMImOTf, (B) BMPyrOTf and (C) EMImOAc with 15 mlmin⁻¹ dried air or nitrogen at dE/dt = 10mVs⁻¹ and RT.

- Highest current density of 15/-18 mAcm⁻² observed for EMImOAc. This is the IL which formed a stable droplet on the Pt/C surface (see Fig. 3). Onset potential for ORR and OER were localized in -0,2-0 V and 1-1,5V potential window, respectively.
- Low current densities for EMImOAc and BMPyrOTf due to (partial) flooding of GDE.

Al deposition/stripping in IL + Al salt mixtures

CV on Al deposition/stripping were performed in different IL/salt mixtures, with Al as counter and reference electrode. EMImCl + 2.3M AlCl₃ (1:1.5) was used as reference electrolyte mixture (Fig. 4).

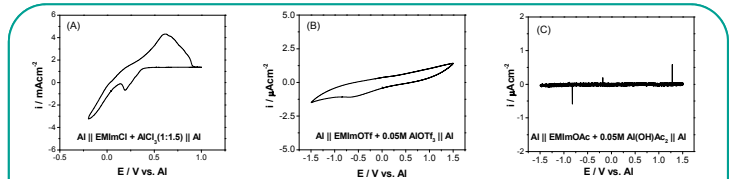


Fig. 4: CVs of Al deposition/stripping in (A) EMImCl+AlCl₃ (1:1.5, 2.3 M), (B) EMImOTf+0.05M AlOTf₃ and (C) EMImOAc + 0.05M Al(OH)Ac₂ at dE/dt = 10mVs⁻¹.

- Activity for metal deposition/stripping in AlCl₃ containing electrolyte only.
- EMImOAc is very hygroscopic and cannot be used with AlCl₃. AlOTf₃ is hardly soluble.

Full-cell test

Charge/discharge profile of Al/air cell with Al as CE and Pt/C as GDE at 100 μA cm⁻².

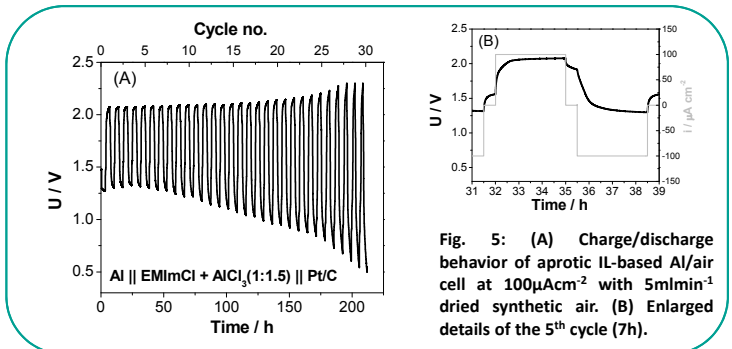


Fig. 5: (A) Charge/discharge behavior of aprotic IL-based Al/air cell at 100μAcm⁻² with 5mlmin⁻¹ dried synthetic air. (B) Enlarged details of the 5th cycle (7h).

- Best cell performance in terms of overvoltage was yielded within the first 6 cycles.
- Quite ideal charge/discharge behavior with an energy efficiency of about 62% after reaching constant cell voltage plateau of 2.1 and 1.3V, respectively, in 5th cycle.
- After 10 cycles, however, cell performance decreased due to moisture in air whereas increase in overpotential is more pronounced during discharge step.

Summary & outlook

- The activity of triflate- and acetate-based IL electrolytes for Al deposition/stripping was clearly lower than that obtained at a chloride-based one.
- Full-cell experiments were performed with conventional EMImCl+AlCl₃ reference mixture over 200h in dried air at 100μAcm⁻² current density
- Future works will focus on increase of charge/discharge capacity, search for alternative air catalysts and optimization of triple-phase boundary.

Acknowledgements

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