

# Development of bifunctional gas diffusion electrodes for metal/air batteries

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## Introduction

Metal/air batteries consist of a metal and an air gas diffusion electrodes (GDE). 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, Si and Zn/air are 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, formation of passive layer such as  $Al(OH)_3$ , 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

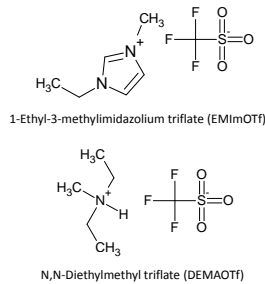


Fig. 1: Chemical structures of EMImOTf and DEMAOTf

(a)protic electrolytes such as EMImCl/ $AlCl_3$ , EMImOTf and DEMAOTf (see Fig. 1) open exciting perspectives especially with respect to suppression of passive layer and carbonate formation. Most of the ILs, however, have a reduced ionic conductivity that limits current density. Average capacity and energy values of most common metal/air systems from references [1-4] are listed below:

		Al	Li	Mg	Si	Zn
Theoretical voltage	V	2,7	3,4	3,1	~ 3	1,6
OCV	V	1,5 <sup>a</sup>	2,9 <sup>b</sup>	2,9 <sup>b</sup>	1,4 <sup>a</sup>	1,6 <sup>a</sup>
Voltage @ 1 nominal	V	1,1-1,4	2,4	1,2-1,4	0,8-1,0	1,0-1,1
Capacity per mass*	Ah/g	3	3,8	2	3,8	0,8
Capacity per volume*	Ah/cm <sup>3</sup>	8,0	2,1	3,8	8,8	5,8
Specific energy	Wh/kg	8146	11246	3942	8470	1363
Energy density	Wh/l	21994	5960	6859	19800	9677

\* anode only, <sup>a</sup> aqueous electrolyte, <sup>b</sup> organic electrolyte

## 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 catalyst and GDE in both ILs and in KOH for reference. Additionally, close cooperation between DFI and associated partner Gaskatel GmbH is planned for GDE manufacturing by calendaring process. Most important challenge consist on finding active catalysts for oxygen reduction (ORR) & evolution (OER) reactions in ILs.

- Oxygen reduction in ILs leads to formation of superoxide ion, stabilized by IL-cation, that can be reduced further in protic ILs to hydrogen peroxide. At Pt electrode, water can be formed [5-7] (see Fig. 2).
- IL electrolyte has to support ORR/OER and metal dissolution/deposition reactions.

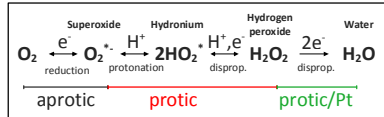


Fig. 2: OER/ORR reaction pathways in ILs

## Perovskite catalyst and GDE preparation

Fig. 3: Catalyst preparation by sol-gel process and GDE manufacturing

- Perovskites  $La_{0.6}Ca_{0.4}CoO_3$  (LCCO) and  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$  (BSCF) have been prepared by sol-gel route from metal nitrate precursors (Figure 2)
- Powders were characterized by XRD and SEM
- 60wt% of the perovskite were mixed with 20wt% carbon + 20wt% PTFE
- GDEs were manufactured by calendaring the catalyst mixture on Ni mesh at Gaskatel

## GDE half-cell stability tests in 7M KOH

- Long-term stability of GDEs for OER/ORR was first evaluated in 7M KOH and synthetic air in a Gaskatel Flex-Cell setup with a Hydroflex  $H_2$  reference electrode (see Figure 4)
- Test protocol consisted of 2.5h OER (charging) @  $10mAc_m^{-2}$ , 30 min break @ 0A, 2.5h (ORR) discharging @  $10mAc_m^{-2}$  and 30 min break @ 0A (see inset in Figure 4(A))
- GDE with  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$  shows up to 60 mV lower OER voltage as compared to GDE with  $La_{0.6}Ca_{0.4}CoO_3$  catalyst, ORR voltage decreases slowly with time
- LCCO-GDE showed stable performance for more than 850h (140 cycles) before measurement was interrupted by pc hardware problems (Fig. 4(B)).

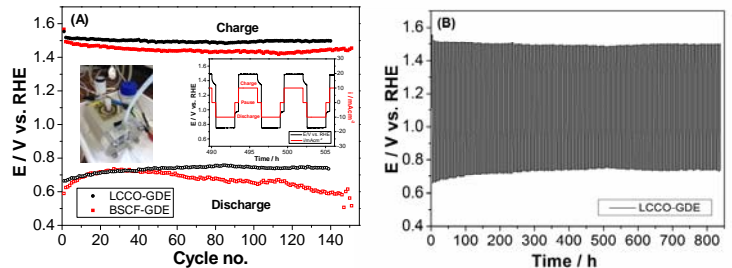


Fig. 4: (A) Comparison of LCCO- and BSCF-GDE activity for OER/ORR in 7M KOH. Insets: Test cell and typical OER/ORR cycles. (B) OER/ORR voltage profile of LCCO-GDE. Air flow :  $30lmin^{-1}$  & air overpressure: approx. 15 mbar.

## Half-cell measurements in IL electrolyte

- Measurements were performed in  $\varnothing 18mm$  EL-Cell Air cells with IL-impregnated  $150\mu m$  glass fibre separator.
- OER/ORR test with  $625\mu m$  Pt foil counter electrode and GDE (Fig. 5(B)).
- Metal deposition/dissolution with Zn/Al 100  $\mu m$  metal foil and Zn/Al metal wire as reference electrode (RE, see Fig. 5(C)).

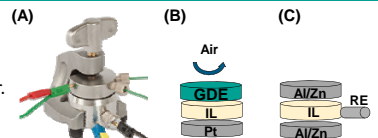
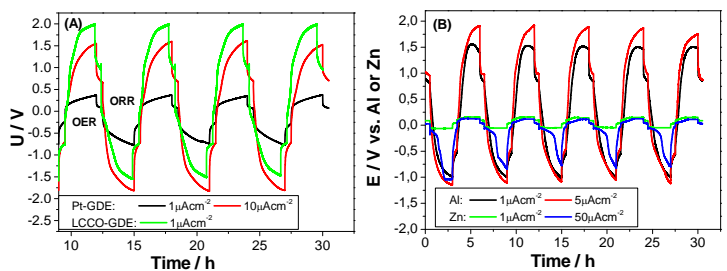


Fig. 5: (A) EL-Cell Air. (B) Setup for OER/ORR and (C) metal dissolution/deposition experiments.



- OER/ORR was investigated in protic DEMAOTf both with LCCO ( $\approx 50 mg_{LCCO}cm^{-2}$ ) and Pt-GDE ( $1mg_{Pt}cm^{-2}$ , 20 wt. % Pt/Vulcan XC72, EC-20-10-7 Quintech) (see Fig. 4(A)).
- Pt-GDE shows a about 10 times higher activity for OER/ORR than LCCO ( $4e^-$  instead of  $2e^-$ -reaction) (see Fig. 6(A)).
- However, activity in IL is lower by factor 1000 compared to KOH electrolyte (see Fig.4). This was attributed to the higher viscosity and lower reactivity of the oxygen species in the ionic liquid.
- In both cases no steady-state voltage was observed.
- Protic IL seems to be the better strategy for OER/ORR in comparison to aprotic IL.
- Zn and Al metal dissolution/deposition was studied in EMImOTf with  $Al(OTf)_3$  or  $Zn(OTf)_2$  (0.01 M, see Fig. 6(B)).
- Zn dissolution/deposition is more favourable in EMImOTf than Al deposition/dissolution.

## Outlook

- Screening of further (a)protic IL electrolytes for both electrodes,
- Adding  $H_2O$  and trifluoromethane sulfonic acid to IL to increase activity for OER/ORR,
- Mixing of LCCO & BSCF perovskites for better GDE performance in KOH is planned.

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