

Gas diffusion electrodes for the Al-Air and Si-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, 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 $\text{Al}(\text{OH})_3$, 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 aprotic electrolyte such as EMI-Cl/ AlCl_3 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 are listed below:

		Al	Li	Mg	Si	Zn
Theoretical voltage	V	2,7	3,4	3,1	~ 3	1,6
OCV	V	1,5 ^a	2,9 ^b	2,9 ^b	1,4 ^a	1,6 ^a
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 ³	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, ^a aqueous electrolyte, ^b organic electrolyte

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 [3] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (3) (1996) 1-5
 [4] T. Reddy, D. Linden, Linden's Handbook of Batteries, McGraw-Hill, 2010

Electrode reactions

- In alkaline media, first dissolution of hydroxides like zincate or aluminates occurs, followed by precipitation and formation of passive layers such as $\text{Al}(\text{OH})_3$ and SiO_2 . ZnO is an exception.
 - The electrode reactions in ILs are quite complex and also depend on purity of the reaction partners. In aprotic ILs like 1-Ethyl-3-methylimidazolium chloride (EMI-Cl) with ZnCl_2 or AlCl_3 , chlorozincates or chloroaluminates are usually obtained. In protic ILs like 1-Ethyl-3-methylimidazolium oligofluorohydrogenate (EMI-(HF)₂3F), SiF_4 reacts with water at the cathode to SiO_2 .
- The main electrode reactions are listed for the discharge process as follows:

	Aqueous alkaline solution	Aprotic (Al/Zn) & protic ionic liquid (Si)
Al-Air	Anode: $4\text{Al} + 16\text{OH}^- \rightarrow 4\text{Al}(\text{OH})_4^- + 12\text{e}^-$ Cathode: $3\text{O}_2 + 6\text{H}_2\text{O} + 12\text{e}^- \rightarrow 12\text{OH}^-$ Overall: $4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} + 4\text{OH}^- \rightarrow 4\text{Al}(\text{OH})_4^-$ Supersaturation: $\text{Al}(\text{OH})_4^- \rightarrow \text{Al}(\text{OH})_3 + \text{OH}^-$	Anode: $\text{Al} + \text{AlCl}_4^- + 3\text{Cl}^- \rightarrow \text{Al}_2\text{Cl}_7^- + 3\text{e}^-$ Cathode: $3\text{O}_2 + 3\text{e}^- + 3\text{EMI-Cl} \rightarrow 3[\text{EMI-O}_2^*] + 3\text{Cl}^-$ Overall: $\text{Al} + \text{AlCl}_4^- + 3\text{O}_2 + 3\text{EMI-Cl} \rightarrow \text{Al}_2\text{Cl}_7^- + 3[\text{EMI-O}_2^*]$
Si-Air	Anode: $\text{Si} + 4\text{OH}^- \rightarrow \text{Si}(\text{OH})_4 + 4\text{e}^-$ $\text{Si}(\text{OH})_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}$ Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ Overall: $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$ [5]	Anode: $\text{Si} + 12(\text{HF})_2\text{F}^- \rightarrow \text{SiF}_4 + 8(\text{HF})_2\text{F}^- + 4\text{e}^-$ Cathode: $\text{O}_2 + 12(\text{HF})_2\text{F}^- + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + 16(\text{HF})_2\text{F}^-$ Reaction with water at the cathode: $\text{SiF}_4 + 2\text{H}_2\text{O} + 4(\text{HF})_2\text{F}^- \rightarrow \text{SiO}_2 + 4(\text{HF})_2\text{F}^-$ Overall: $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$ [6]
Zn-Air	Anode: $2\text{Zn} + 8\text{OH}^- \rightarrow 2\text{Zn}(\text{OH})_4^{2-} + 4\text{e}^-$ $2\text{Zn}(\text{OH})_4^{2-} \rightarrow 2\text{ZnO} + 4\text{OH}^- + 2\text{H}_2\text{O}$ Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ Overall: $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$	Anode: $\text{Zn} + \text{Zn}_2\text{Cl}_6 + 2\text{Cl}^- \rightarrow \text{Zn}_3\text{Cl}_7^- + 2\text{e}^-$ Cathode: $2\text{O}_2 + 2\text{e}^- + 2\text{EMI-Cl} \rightarrow 2[\text{EMI-O}_2^*] + 2\text{Cl}^-$ Overall: $\text{Zn} + 2\text{O}_2 + \text{Zn}_2\text{Cl}_6 + 2\text{EMI-Cl} \rightarrow \text{Zn}_3\text{Cl}_7^- + 2[\text{EMI-O}_2^*]$

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Objectives

- 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 of the respective institutions are briefly resumed in following table. Additionally, close cooperation between DFI and associated partner Gaskatel GmbH is planned for GDE manufacturing by calendering process.

TU Clausthal	Electrochemistry of anode materials, macroporous Al and Si electrodes
TU Berlin	Production of microstructured electrodes test cell arrays for statistical characterization (electrolyte additives, mixtures)
FZ Jülich	Electrochemistry, 'in situ' characterization of electrode-electrolyte interface, transport and transformation reactions, synthesis of Al/Si alloy electrodes
DFI	Development of catalysts and gas diffusion electrodes for the air electrode of the metal-air batteries
Iolitec	Synthesis and development of ionic liquids

Bifunctional catalysts

Some of the following perovskites will be investigated in this work:

- LaNiO_3 and $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ have already exhibited high activity for both oxygen reduction reaction (ORR) during discharge and oxygen evolution reaction (OER) during charge in alkaline solutions [1-2]. Stability of LaNiO_3 should be improved.
- Encouraging results were reported in aprotic Li/O_2 cell with LaNiO_3 [3], $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ [4], $\text{La}_{0.75}\text{Sc}_{0.25}\text{MnO}_3$ perovskites and ZnCo_2O_4 spinel [6].
- Other possible catalysts: $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$, TiC [7]...

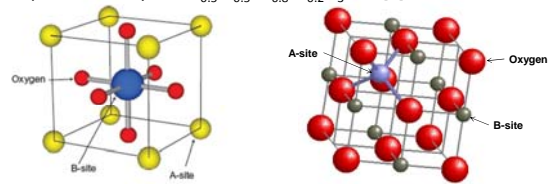
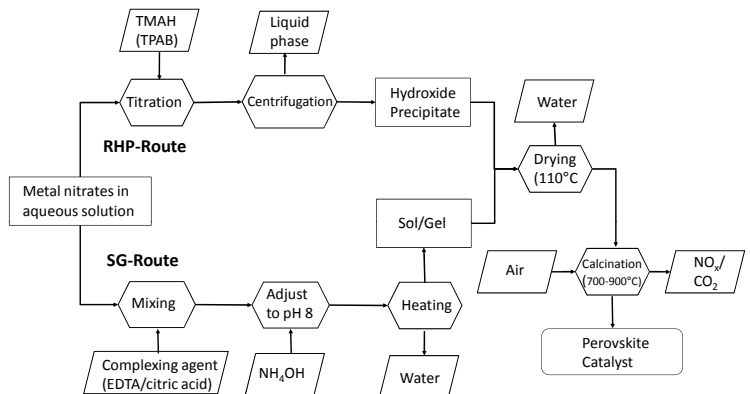


Fig. 1: (Left) Atomic structure of ABO_3 perovskite, (right) AB_2O_4 spinel structure.

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 [4] Y. Zhao et al., Proc. Natl. Acad. Sci. 109 (2012), 19569 [5] J.-I. Xu, Angew. Chem. Int. Ed. 52 (2013), 3887 [6] T.-F. Hung et al., Nanoscale, 2013, 5, 12115
 [7] M. M. Ottakam Thoity, Nature Materials, 12 (2013) 1050

Catalyst preparation

- Bifunctional perovskite catalysts will be produced by either reverse homogeneous precipitation (RHP) or sol/gel (SG) process depending on the solubility of the metal nitrate precursors and desired particle size as follows:



- Since electronic conductivity of the perovskite catalysts is usually insufficient, carbon material has to be added. The influence of the carbon content on the activity and stability of the catalyst with respect to ORR and OER will be examined.

GDE properties and fabrication

- Preparation of the GDE will be performed either by ultrasonic spray coating (USI Prism) of the catalyst ink on a carbon gas diffusion layer or by calendering (Vogt W80T) a powder/PTFE mixture onto a Ni/Au current collector. Finally a PTFE membrane should protect against electrolyte leak.

- Since GDE design regarding porosity, conductivity and hydrophobicity depends on material interaction with electrolyte and atmosphere, the different Al/Si/Zn-based systems must be individually considered and optimized.



Fig. 2: (Left) Spray coating machine and (right) calender

Catalyst characterisation techniques

- Catalysts will be characterized by physical methods XRD, TEM and SEM/EDX.
- Electrochemical activity of the catalyst towards ORR/OER will first be characterized by half-cell measurements with rotating ring-disc electrode (RRDE) and (GDE-cell) and finally in laboratory metal/air cell (EI-cell).

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