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Bundesministerium für Bildung und Forschung

Chemical Technology

Rechargeable Al/Air battery with $AlCl_3$-containing electrolyte

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Motivation & Challenges

- Metal/air batteries such as Al/Air (8040 vs. 2046 AhL^{-1} for Li-ion) are potential candidates for sustainable energy storage applications
- High specific energy density possible due to gas diffusion electrode (GDE)
- Al is highly abundant and non-toxic
- Electrolyte should
  - be active for oxygen reduction/evolution (ORR/OER) and aluminum deposition/dissolution and electrochemically stable
  - allow triple-phase-boundary formation in GDE (contact angle > 110°C)
  - be water-free to avoid aluminum passivation

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Strategy & Electrode Reactions

- Use of ionic liquid (IL) or deep eutectic solvents (DES) for aluminum deposition/dissolution from water-free lewis-acidic $AlCl_3$-containing electrolytes
- Assumed electrode reactions in EMImCl+$AlCl_3$:

  Anode: $Al + 7\ AlCl_4^- \rightarrow 4\ Al_2Cl_7^- + 3\ e^-$

  Cathode: $O_2 + EMIm^+ + 1\ e^- \rightarrow [EMIm\text{-}O_2^*]$ [1-2]

  Overall: $Al + 7\ AlCl_4^- + 3\ O_2 + 3\ EMIm^+ \rightarrow 4\ Al_2Cl_7^- + 3\ [EMIm\text{-}O_2^*]$

  Possible side-reactions:

  Cl_2 evolution during charging. $AlCl_3$ reacts to Al_2O_3 with residual moisture

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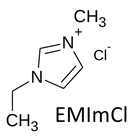
Experimental

$AlCl_3$-based electrolyte preparation

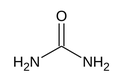
- Electrolytes were prepared by mixing 1-ethyl-3-methylimidazolium chloride (EMImCl), urea or acetamide with $AlCl_3$ in a glovebox under water-free inert gas (H_2O & O_2 < 0.1 ppm)
- Reactions:

  $EMImCl + 2AlCl_3 \rightarrow [EMIm]^+ + Al_2Cl_7^-$

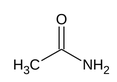
  $RNH_2 + 3AlCl_3 \rightarrow [AlCl_2 \cdot RNH_2]^+ + Al_2Cl_7^-$ [3]



EMImCl



Urea



Acetamide


Acetamide + $AlCl_3$ (1:1.6)

Cell set-up for electrochemical measurements

- Commercial ECC-Air cell
- Electrode area: 2.54 cm^2 (∅ 18 mm)
- GDE catalyst: Pt/C (1 mg_{Pt} cm^{-2})
- Pyrolytic graphite (PG) for half-cell measurements
- 300 µl electrolyte
- 1.55 mm glass fiber separator
- Dried synthetic air (2 ml min^{-1}, 15 mbar overpressure)


ECC-Air cell

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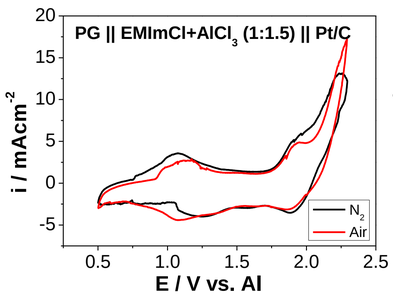
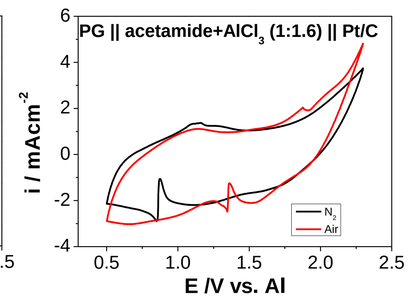
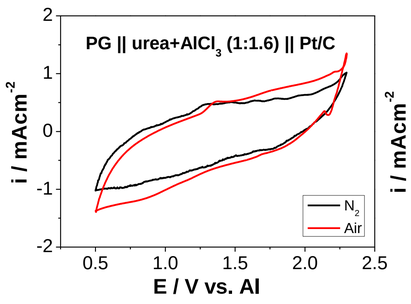
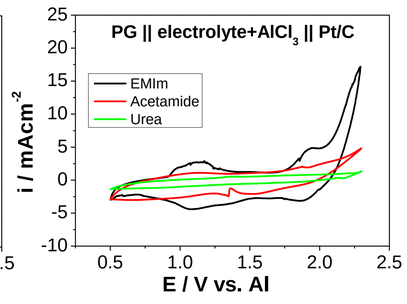
Results

Half-cell tests: ORR & OER at GDE





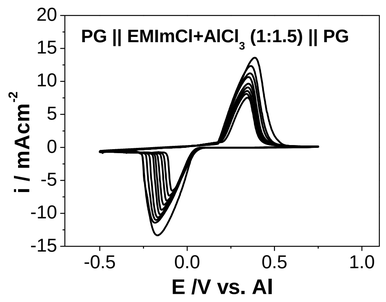


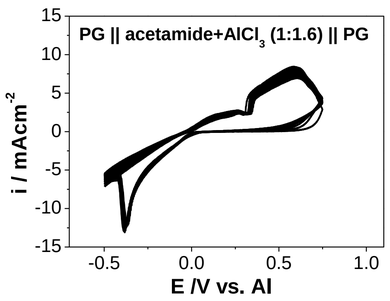


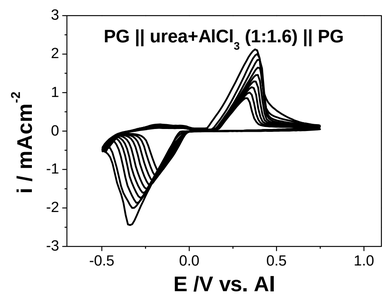
CVs at Pt/C with air or N_2 @ dE/dt = 10 mV s^{-1}

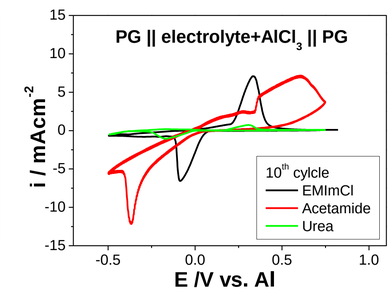
- Highest current densities with EMImCl+$AlCl_3$
- However, onset potentials of ORR/OER are not well-defined: presumed values for ORR 1-1,5 V and for OER 1,75 – 2.2 V vs. Al
- Relative low ORR values are an indication for absence of triple-phase-boundary (TPB)

Half-cell tests: Al stripping & deposition on PG





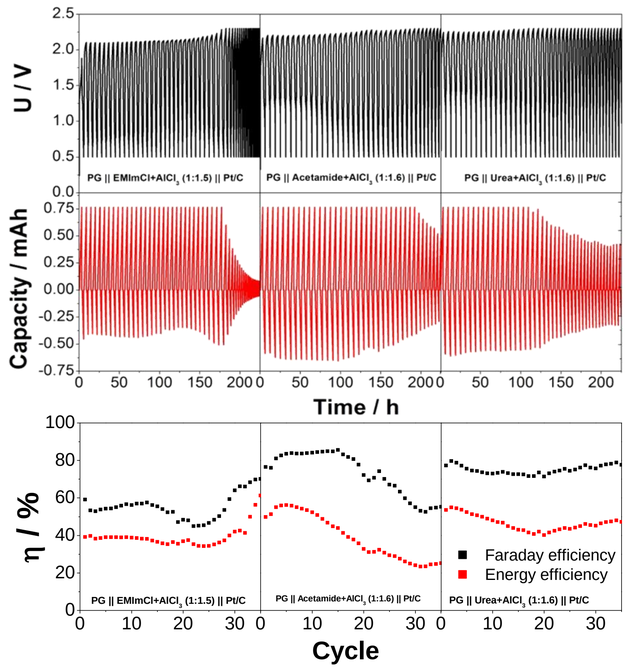




CVs at PG @ dE/dt = 10 mV s^{-1}

- All studied electrolytes favor Al deposition/stripping
- EMImCl+$AlCl_3$ shows highest reversibility for Al-deposition/stripping on pyrolytic graphite
- In acetamide, redox peaks are asymmetric and high overpotentials for Al-stripping are visible

Full-cell tests



Cell voltages, capacities and efficiencies

- 15 stable charge/discharge cycles (3h each) possible at 100 µA cm^{-2} with cut-off voltages of 2.3V and 0.5V
- Average $\eta_{Faraday,\ 15cycles}$: acetamide 82%, urea 75% & EMImCl 56%
- Average $\eta_{Energy,\ 15cycles}$: acetamide 53%, urea 50% & EMImCl 39%

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Conclusion & Outlook

- Feasibility of reversible Al/air battery with EMImCl, acetamide and urea + $AlCl_3$ (300 µAh cm^{-2} for 15 cycles in extremely dry air) was demonstrated
- Cells with cheap DES electrolytes (acetamide & urea) show higher current and energy efficiencies than those with expensive IL (EMImCl)
- Screening of further aprotic ILs or DES that favor TPB formation

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Literature

[1] C.J. Allen, J. Phys. Chem. C, 116 (2012) 207555

[2] C. Lu et al., J. Phys. Chem. C, 118 (2014) 3393

[3] H.M.A. Abood et al., Chem. Commun., 2011, 47, 3523–3525