DECHEMA FORSCHUNGSINSTITUT

Tuning a layered MnO_2 cathode for the Al-ion battery

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Introduction

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- High demand for small to medium scale electrical energy storage
- Lithium-ion batteries show capacity, cost and safety limitations
- Search for the next battery generation is imperative
- One alternative: aluminium metal batteries
  - High volumetric capacity: 8045 Ah/L (2061 Ah/L Li metal)
  - Great abundance: 8 wt.% of earths crust
  - Low price: well established aluminium processing and recycling
  - Reversible plating and stripping of aluminium at room temperature in water-free EMIMCl+$AlCl_3$ ionic liquid.

Motiviation

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Search for performing and stable Al-ion intercalating cathode:

- Olivine (tunnel) MnO_2: inhibited by blocking of 1D channels
- Layered MnO_2 (Birnessite): Pores not accessible to large Al-ions
  - Al^{3+}: 0,1 nm
  - $AlCl_4^-$: 0,52 – 0,63 nm
  - $EMIM^+$: 0,54 nm
- Spinel Mn_3O_4: inactive species

Mn_xO_Y	Ion transport	Capacity mAh/g	Pore size nm
Olivine	1D	170-230	≥ 0,28
Layered	2D	230-300	≥ 0,28
Spinel	3D	0	-

Tab. 1 - Manganese oxides for the cathode of Al-ion batteries

Approach

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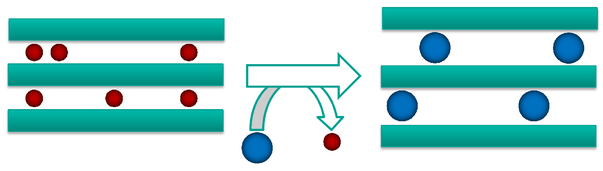
Layered MnO_2 with adjustable pore sizes

- Increase 2D pore size through pillar size though ion/pillar exchange



- Optimize for low volume and high capacity

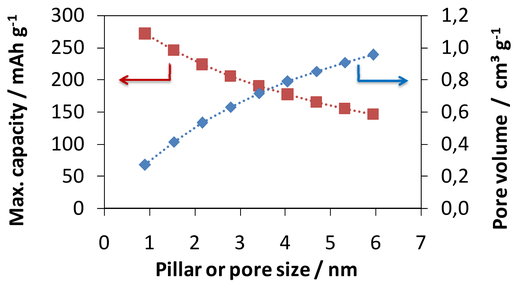


Fig. 2 – Theoretical δ-MnO_2 pore volume and capacity

Synthesis of δ-MnO_2

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Nanosheet synthesis

- One pot synthesis at room temperature
- Resulting in stable nanosheet dispersion

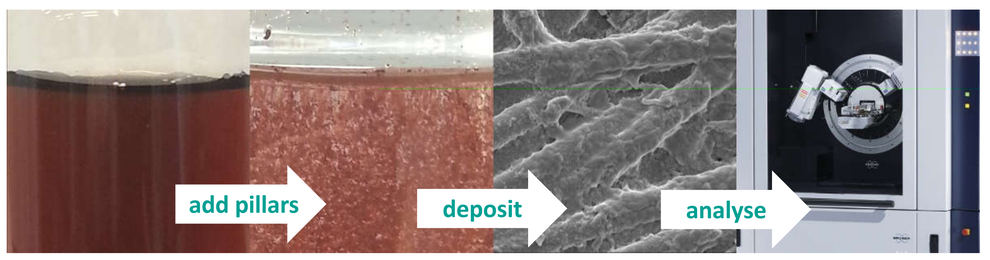

Fig. 3 – Synthesis of nanosheets: dispersion, flocculation with K-ion pillars, deposition on carbon fiber paper, XRD analysis on phase and purity

- Addition of pillars:
  - Potassium: 0,28 nm
  - Graphite particle: 10 nm
  - Carbon black: 60 nm
- XRD analysis:
  - δ-MnO_2 cathodes

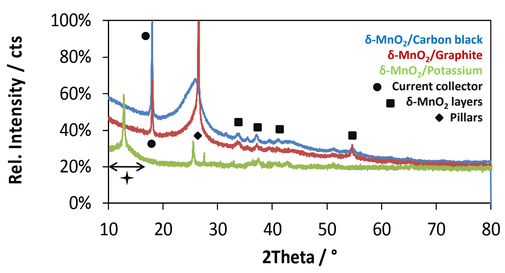

Fig. 4 – XRD analysis of Graphite and Carbon black pillared δ-MnO_2

- Incorporation of large pillars confirmed by absence of peaks in small pillar range (+)
- Pillar to layer ratio has to be optimized

Battery testing

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Measurement properties

- Full and half cell measurements
- Cell composition:
  - Al || EMIMCl+$AlCl_3$ || δ-MnO_2
  - Cathode: δ-MnO_2 + graphite pillar
  - Reference electrode: aluminium
  - Electrolyte ratio: (1:1.5)
  - Coin cell setup: El-Cell

Cyclovoltametry measurements

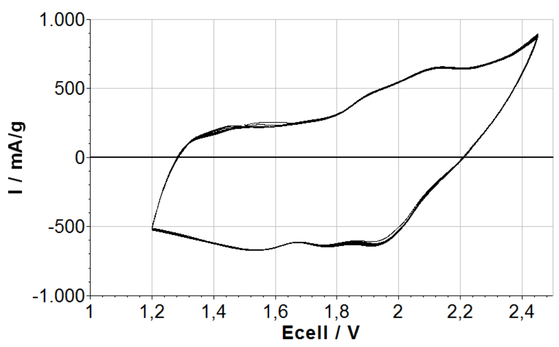

Fig. 5 – CV: 10 mV/s; vs. Al. ref.; Cycle 130-140; A-162-d6

Charge/discharge experiments

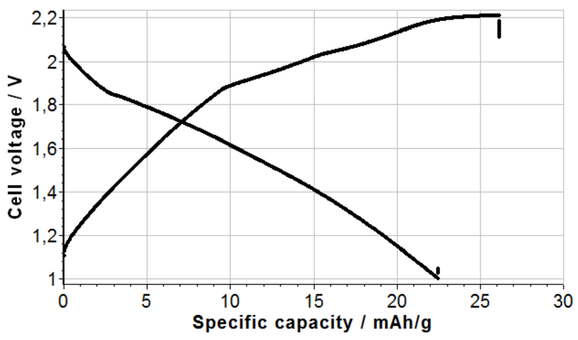

Fig. 6 – Cycling at C10; Cycle 24_A-162-f1; total mass of layer/pillar structure: 17 mg

Performance results

- CV:
  - High currents verify good ion accessibility into layers
  - Clearly visible redox activity
- Charge/discharge
  - Max. capacity: 22,5 mAh/g
  - Good coulombic efficiency: 87%
  - Mean cell voltage: >1.5 V
  - More than 110 cycles

Conclusion

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- Successful synthesis of δ-MnO_2 nanosheets at room temperature
- Pore size in layered manganese oxides is adjustable through addition of different pillars
- Synthesis parameter to be adjusted: pillar to layer ratio and pillar size
- First electrochemical results suggest high surface area and good ion accessibility into layer/pillar structure
- Resonable cell voltage of 1.5 V achieved

Literature

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- M. S. Whittingham, Sol. State Ionics, 2000, 131, 109
- L. Z. Wang – Adv. Mater. 2004, 16, 1412

ALION