

# Novel cathode materials for the Al-ion battery

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## Introduction

The worldwide lithium resources are sufficient to supply the Lithium-ion battery (LIB) production for the next decade. Later on, the overall storage demand, comprising EV, grid storage and mobile devices will be larger than the amount of lithium needed. Therefore other battery storage concepts are under investigation. These post Lithium-ion batteries (PLIB) should provide equal or higher capacity, while being cheaper, based on more abundant materials and less prone to hazardous decomposition.

Such a PLIB technology is the Aluminium-ion or Aluminium-metal battery. Aluminium is providing a variety of beneficial attributes such as abundance (8 wt.% of earth's crust, low cost, large scale manufacturing, processing and recycling, as well as high capacity (2.98 Ah/g and 8.05 Ah/cm<sup>3</sup>) compared to lithium (3.86 Ah/g and 2.06 Ah/cm<sup>3</sup>).

Due to the high capacity of the aluminium metal the battery of choice should comprise an aluminium metal anode, as well as an aluminium ion intercalating cathode. This approach has been pursued by a variety of scientists using graphite and vanadium oxide based cathodes.<sup>2-6</sup>

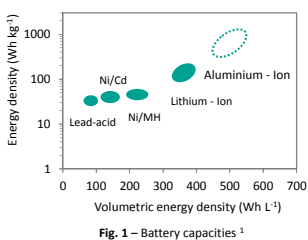


Fig. 1 – Battery capacities<sup>1</sup>

## Cathode manufacturing

For the coating of the sol-gel synthesized oxides an ink was prepared, that comprised components of table 1. C65 provides conductivity, while KS6L additionally stabilizes the coating mechanically.

Table 1 – Cathode composition

| Type                | Ratio                                   |
|---------------------|---|
| Active material     | AlMn <sub>2</sub> O <sub>4</sub> 80 %   |
| Binder              | PTFE 10 %                               |
| Conductive additive | C65 (carbon) 5 %<br>KS6L (graphite) 5 % |
| Current collector   | carbon paper -                          |

Fig. 3 – (Top) Spray & (bottom) doctor blade coated electrode

## Synthesis of aluminium manganese oxides

The synthesis of Al<sup>3+</sup> intercalating oxides has been carried out via sol-gel method, as described in figure 2, followed by multiple calcination steps, milling and coating. The improvement of synthesis parameters to yield higher activity nano-scale oxides is ongoing.

The abundance of manganese (0.95 wt.% of earth's crust) as well as the theoretical high capacity of the cubic spinel aluminium manganese oxide based cathodes (400 mAh/g for AlMn<sub>2</sub>O<sub>4</sub>) made the manganese oxides our active material of choice.

A cell voltage of 2.65 V (vs. Al) results in a high theoretical energy density of 1060 Wh/kg.<sup>7,8</sup>

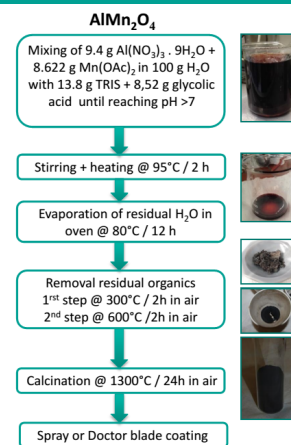
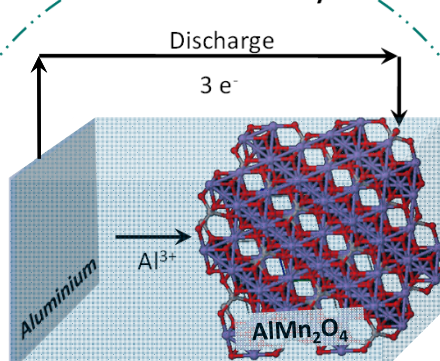


Fig. 2 – Sol-gel synthesis route

## Al - Metal Battery



Electrolyte: 2 AlCl<sub>3</sub> + EMIMCl → EMIM<sup>+</sup> Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>  
 Cathode: λ-Mn<sub>2</sub>O<sub>4</sub> + 4 Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> + 3 e<sup>-</sup> → AlMn<sub>2</sub>O<sub>4</sub> + 7 AlCl<sub>4</sub><sup>-</sup>  
 Anode: Al + 7 AlCl<sub>4</sub><sup>-</sup> → 4 Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> + 3 e<sup>-</sup>  
 Net: λ-Mn<sub>2</sub>O<sub>4</sub> + Al → AlMn<sub>2</sub>O<sub>4</sub> (+2.65 V vs. Al)

## XRD analysis

The intercalation of aluminium ions in manganese oxide based cathodes takes place in either cubic spinel or layered oxides. During charging (deintercalation of Al ions) the cubic spinel structure is prone to Jahn-Teller distortion – forming a less active tetragonal spinel phase. Fig. 4 shows spectra of cubic spinel oxide, all cathode components, as well as the spinel based cathode. Post mortem analysis does not show any crystal phase changes.

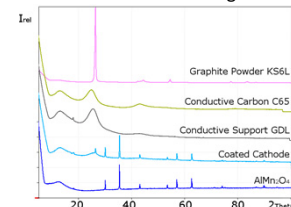


Fig. 4 – XRD spectra of a cathode and all cathode components

## Half-cell measurements

These experiments aimed to identify charge/peak contribution of AlNiMnO<sub>x</sub> intercalation electrode compounds to cyclic voltammograms (CV). All measurements were performed by using pyrolytic graphite (PG) foil as anode (acts as support for Al<sup>3+</sup> deposition), EMIMCl:AlCl<sub>3</sub> (1:1.5) as electrolyte and AlNiMnO<sub>x</sub> or AlMn<sub>2</sub>O<sub>4</sub> as Al intercalation electrode.<sup>9-11</sup> The former has shown a high redox stability and was used here as reference material for peak identification of AlMn<sub>2</sub>O<sub>4</sub>.

Table 2 – CV analysis results; CV peaks are colour coded according to component

| Fig. 5 | Cathode composition                  | Coulombic Efficiency | CV Peaks V <sub>ox</sub> / V <sub>red</sub> | CV Capacity mAh/g |
|--------|--------------------------------------|----------------------|---|-------------------|
| A      | AlNiMnO <sub>x</sub> 80%             | 90.9 %               | 2.0 / 1.9                                   | 2.2               |
|        | C65 10%                              |                      | 0.75 / 0.4                                  |                   |
|        | KS6L 0%                              |                      |   |                   |
| B      | AlNiMnO <sub>x</sub> 80%             | 107.0 %              | 2.2 / 2.0                                   | 4.2               |
|        | C65 0%                               |                      | 2.0-2.4 / 2.0                               |                   |
|        | KS6L 10%                             |                      | 1.8/1.7-1.0                                 |                   |
| C      | AlNiMnO <sub>x</sub> 80%             | 85.0 %               | 2.2 / 2.1                                   | 7.9               |
|        | C65 5%                               |                      | 0.7 / -                                     |                   |
|        | KS6L 5%                              |                      | 2.3 / 2.0                                   |                   |
| D      | AlMn <sub>2</sub> O <sub>4</sub> 80% | 97.3 %               | 2.3 / 2.1                                   | 12.6              |
|        | C65 5%                               |                      | 1.9 / 1.8                                   |                   |
|        | KS6L 5%                              |                      | 1.8 / 1.7                                   |                   |

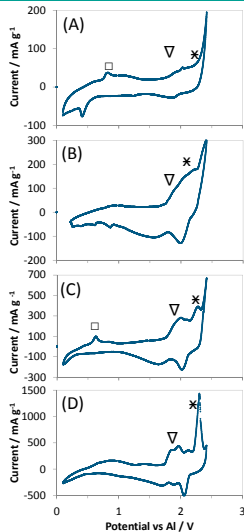


Fig. 5 – CVs at 10 mV/s

- Peak at 0.75-0.4V (□) was assigned to carbon C65 redox activity.
- Similar CV profile for AlNiMnO<sub>x</sub> (C) and AlMn<sub>2</sub>O<sub>4</sub> (D).
- No indication for Ni redox reactions (Ni<sup>2+</sup>/Ni<sup>4+</sup> ~3,25V vs. Al).
- (Δ) and (\*) peak may be assigned to Mn<sup>3+</sup>/Mn<sup>4+</sup> and Mn<sup>2+</sup>/Mn<sup>4+</sup> redox couple, respectively, whereas reactions usually occur at higher potentials (Mn<sup>3+</sup>/Mn<sup>4+</sup> ~2,6V and Mn<sup>2+</sup>/Mn<sup>4+</sup> ~2,89V vs. Al). This has to be elucidated by XPS analysis.
- The AlMn<sub>2</sub>O<sub>4</sub> spectra show higher coulombic efficiency as well as higher specific current and capacity than AlNiMnO<sub>x</sub> one.

## Full-cell battery cycling

For the cycling experiments in the CCCV mode the upper cut of voltage was set to 2.42 V (vs. Al) to avoid electrolyte decomposition at 2.5 V. The lower cut off voltage was set to 0.5 V.

- The AlMn<sub>2</sub>O<sub>4</sub> cubic spinel oxide based cell has shown moderate capacity (50 mAh/g).
- Rather flat discharge voltage plateau in 2.2–1.5 V range can be observed.
- The lower discharge plateau (0.5-0.4V) can be attributed to the C65 redox activity. Additionally, the unfavoured reduction of Mn<sup>2+</sup> to elemental manganese could take place.

- For the first time, a reversible behaviour was observed for about 100 cycles. For better clarity, only 31 cycles are depicted in Fig. 6 b.

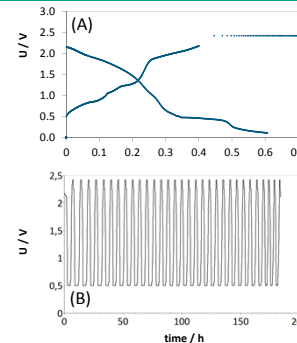


Fig. 6 – Full-cell measurements

## Resumé and outlook

The cubic spinel AlMn<sub>2</sub>O<sub>4</sub> oxide is a promising aluminium ion intercalation material. Half cell measurements clearly highlight the activity and reversibility of the reaction. Full cell cycling confirms a low but stable capacity. An increased electrolyte stability (2.7 V vs. Al) as well as an improved nano-scale oxide synthesis should further raise the overall activity.

## Acknowledgements

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<sup>1</sup> J. W. Fergus, J. Phys. Chem. C, 2010, 114, 939-954; <sup>2</sup> L. D. Reed, J. Electrochem. Soc., 2013, 160, A915-A917; <sup>3</sup> M. C. Lin et al., doi: 10.1038/nature14340; <sup>4</sup> J. V. Rani et al., J. Electrochem. Soc., 2011, 158, A1781-A1784; <sup>5</sup> W. Wang et al., Sci. Rep., 2013, 3, 3383; <sup>6</sup> N. Jayaprakash et al., Chem. Commun., 2011, 47, 12610 ff; <sup>7</sup> M. P. Paranthaman, 218th ECS Meeting, #314; <sup>8</sup> G. M. Brown, US 2012/0082904 A1; <sup>9</sup> Y. Nakayama et al., Phys. Chem. Chem. Phys., 2015, 17, 5758; <sup>10</sup> G. Kamath et al., Phys. Chem. Chem. Phys., 2014, 16, 20387; <sup>11</sup> S. Z. El Abedin et al., EC. Com. 12 (2010) 1084-1086;