A novel battery concept – a joint European effort
Development of intercalation electrodes for the aluminium-ion battery

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Introduction

Lithium-Ion batteries have without doubt conquered numerous market segments due to their excellent storage properties. Their high capacity (300-450 Wh kg^{-1}) is unmatched and the achieved cycle stability hasn´t been realized with any other battery technology. [1]

Li-ion technology relies on a broad variety of electrode materials like $LiCoO_2$, NiMnCo, NiCoAl, $LiMn_2O_4$ and $LiFePO_2$ that have been developed for a multitude of commercial applications, such as electronic devices, electric vehicles & backup systems. [2,3]

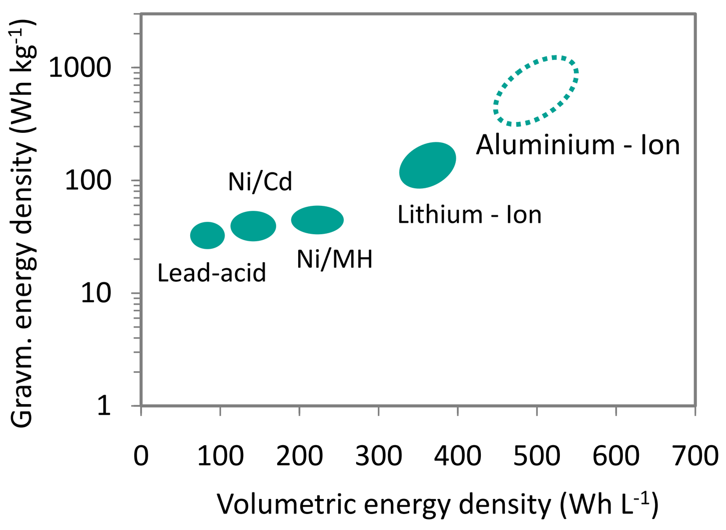


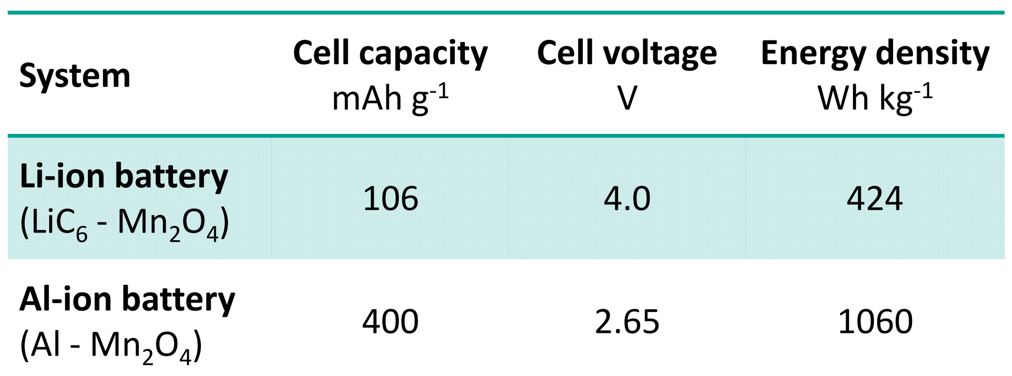
Fig. 1 – Battery technologies. [5]

Nonetheless Li-ion technology is facing limitations in case of overcharging/discharging and/or overheating, as well as short-circuit. These may lead to decomposition of both – the electrodes and the electrolyte – and/or consecutive cell ignition (thermal runaway). Aging of the electrodes has been observed through leaching of soluble ions (Mn, Fe, Ni, Co) into the electrolyte. [3]

[1] L. D. Reed, J.ECS,160 (6) A915-A917 (2013); [2] M. Lowe, Duke University, 05.10.10; [3] J. W. Fergus, J.PS 195 (2010) 939-954; [4] J. V. Rani *et al.*, J.ECS 160 (10) A1781-A1784 (2913); [5] , M. P. Paranthaman, 218th ECS Meeting, #314;

Aluminium Ion Batteries

Within the last decade, the search for post Li-ion battery systems has been intensified. Mg^{2+} and Ca^{2+} as well as Zn^{2+}, Na^{2+} and Al^{3+} have been discussed as substitutes, due to their polyvalence. [4]



System	Cell capacity mAh g^{-1}	Cell voltage V	Energy density Wh kg^{-1}
Li-ion battery (LiC_6 - Mn_2O_4)	106	4.0	424
Al-ion battery (Al - Mn_2O_4)	400	2.65	1060

Table 1 – Theoretical data: Al-ion vs. Li-ion battery based on the weight of electrode materials.[5]

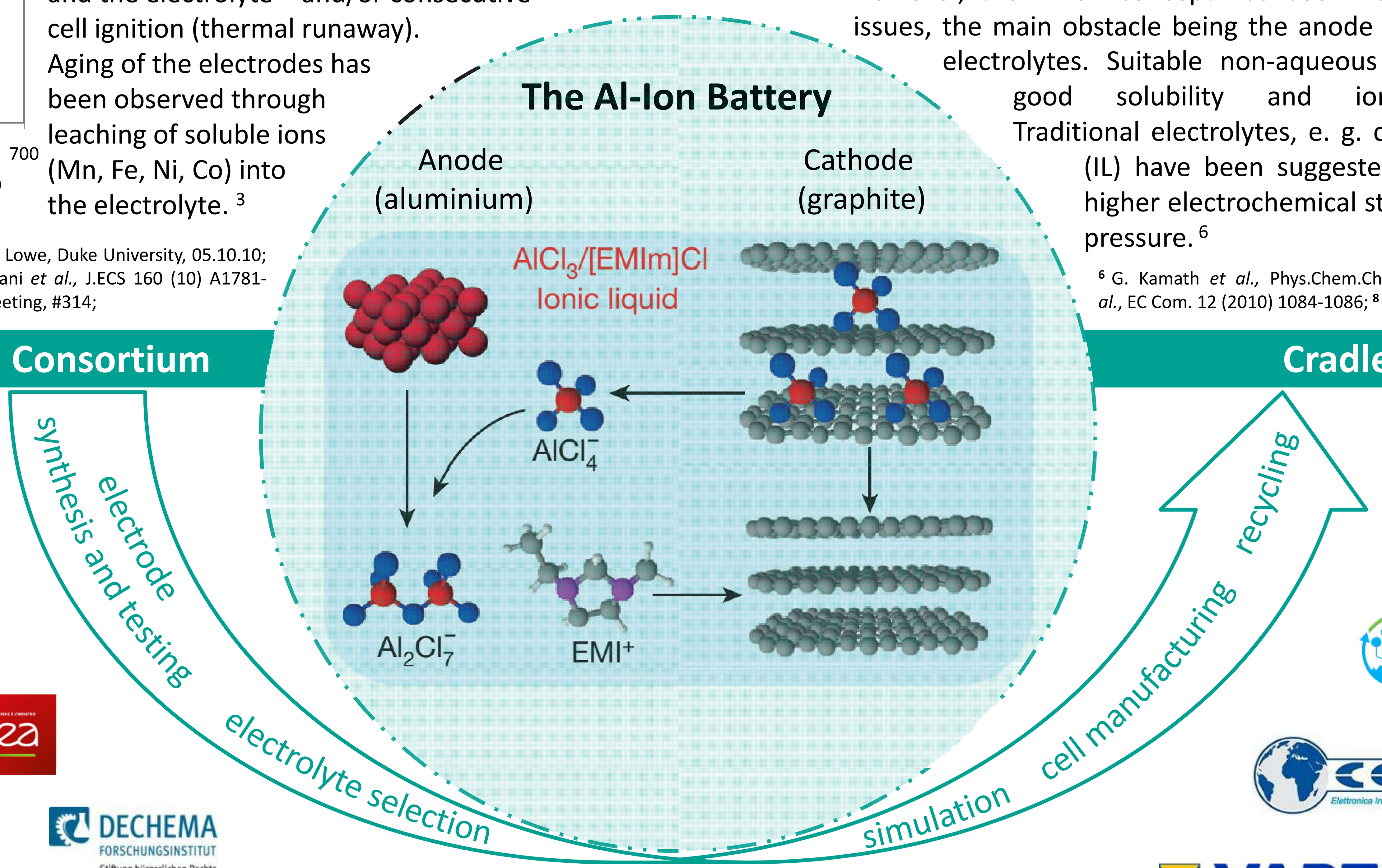
Especially the trivalent aluminium cation is an interesting candidate exhibiting a remarkable theoretical energy density of 8140 Wh kg^{-1} (vs. 1462 Wh kg^{-1} for Li-ion). Aluminium is abundant and inexpensive, resulting in cost savings of $ 3000 per electrical vehicle. [5]

However, the Al-ion concept has been held back by some challenging issues, the main obstacle being the anode passivation (Al_2O_3) in aqueous electrolytes. Suitable non-aqueous electrolytes should combine good solubility and ion conductivity for Al^{3+}. Traditional electrolytes, e. g. carbonates failed. Ionic Liquids (IL) have been suggested as electrolytes, exhibiting a higher electrochemical stability as well as a lower vapor pressure. [6]

[6] G. Kamath *et al.,* Phys.Chem.Chem.Phys.,2014,16,20387; [7] S.Z. El Abedin *et al.*, EC Com. 12 (2010) 1084-1086; [8] M. C. Lin *et al.*, doi: 10.1038/nature14340;

ALION – A European Consortium

Cradle to Cradle



State of the Art

The successful deposition of Al-metal with IL (EMIM-Cl and EMIM-TFO) has been first demonstrated by S. Z. El Abedin *et al*.. Kamath *et al.* reported a reasonably good ionic conductivity of Al^{3+} in IL (0.14 S cm^{-1}), due to the lower stability of ion-solvent complexes. Based on these results different electrode materials have been tested successfully. [6,7]

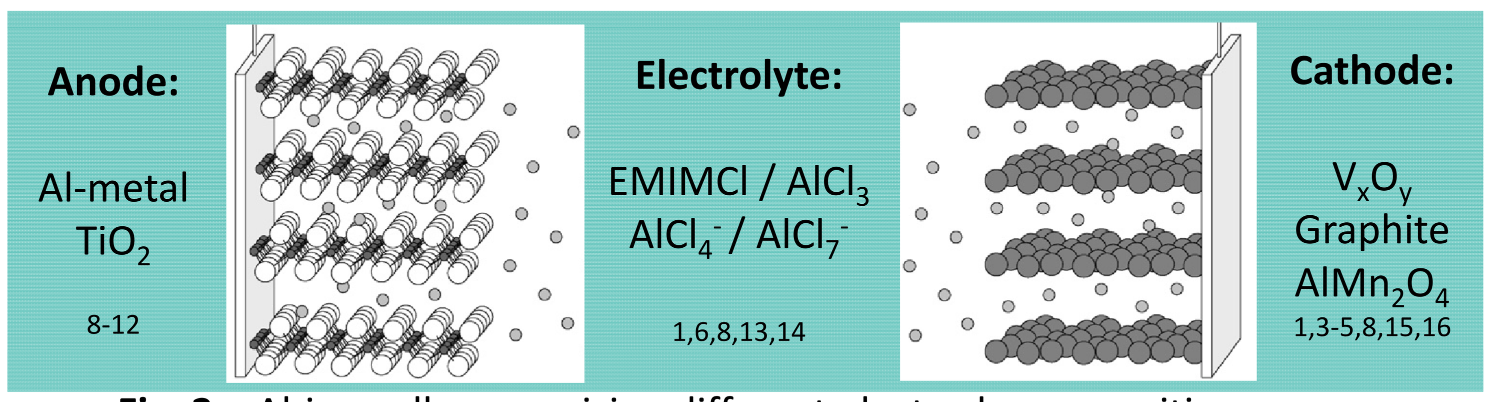


Fig. 2 – Al-ion cell - comprising different electrode compositions.

Some of these batteries show an exceptional performance and prove the applicability of the IL-based Al-ion battery concept. [1]

The best results so far have been published by Lin *et al.* using a battery comprising an aluminium metal anode, the electrolyte EMIMCl-$AlCl_3$ and graphitic foam as cathode. They presented a mechanically bendable battery, exhibiting a superior capacity of 3000 W kg^{-1}, while lasting 7500 cycles – without decay. [8]

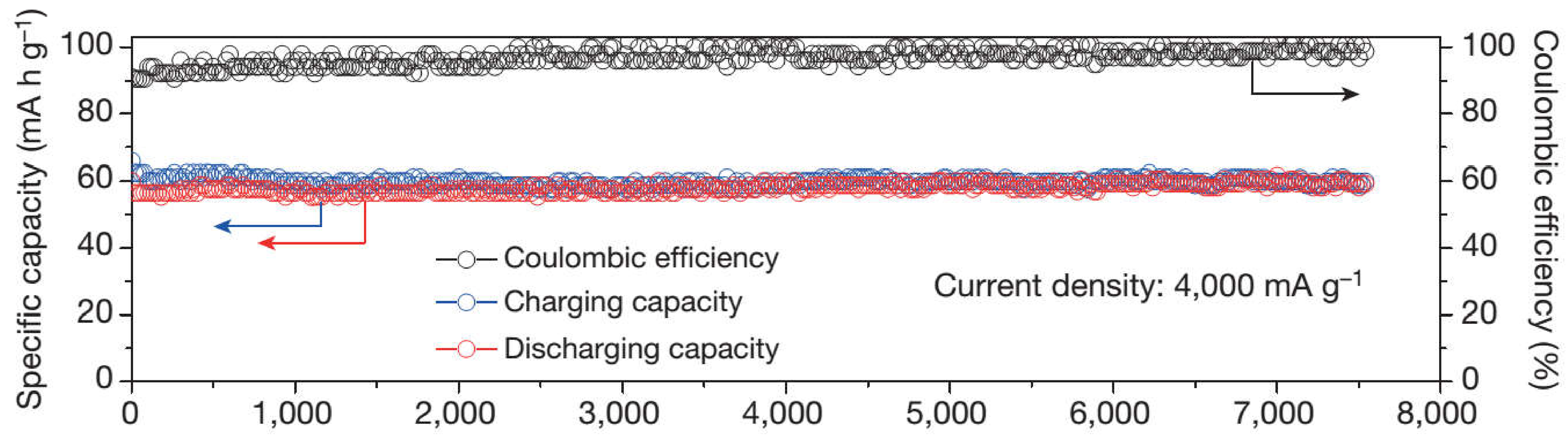


Fig. 3 – Performance stability of an Al-ion cell - without decay. [8]

DFI - Objective

Within the ALION project, DFI activities focus on the development of intercalation materials for Al-ion batteries. This search is based on the vast amount of stable layered, spinel or olivine oxide structures, which have been applied as electrode materials within Li-ion battery technologies.

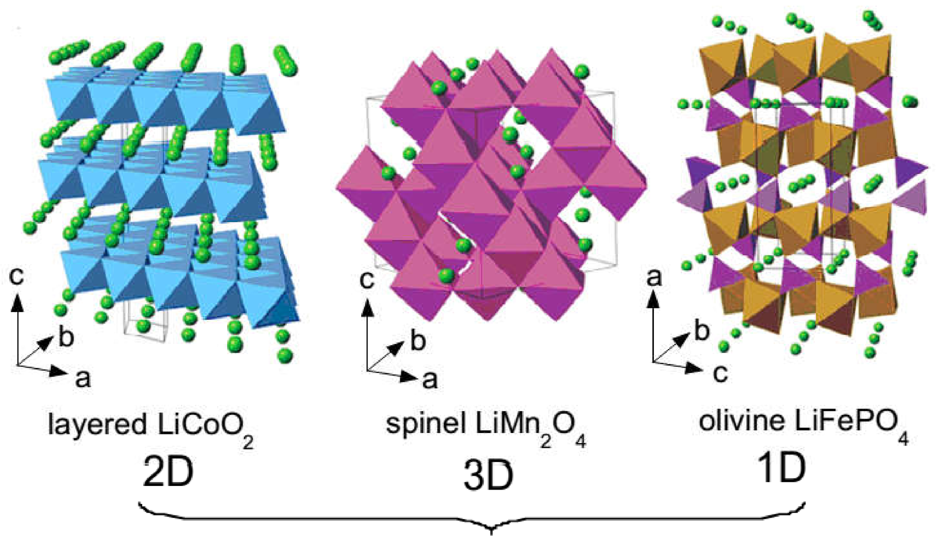


Fig. 4 – Dimensionality of ion transport. [17]

The preparation of intercalation materials is proceeding mainly via the sol-gel route. Cathode materials like MnO_2, $AlMn_xO_{x+2}$, $AlNi_xO_{x+2}$, will be joined with different additives and combined with anodes consisting of $AlTiO_2$, graphite, or pure aluminium metal. Different Ionic Liquids and their effect on battery capacity, stability and general performance will be examined.

Electrode reaction kinetics and battery testing will be performed using cyclic voltammetry (half cell), battery cycling and impedance spectroscopy (full cell). In-depth chemical and physical analysis of as-prepared and aged electrode materials will be conducted by XRD, REM, WDX and Raman. Corrosion stability and post – mortem studies of the electrodes and the electrolyte will be investigated by IC-ICP-MS.

Acknowledgements

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[9] Y. Liu *et al.*, EC Acta, 143 (2014) 340-346; [10] Y. J. He *et al*., J.Mat.Chem A, 2014,2,1721; [11] W. Wang *et al.* Sci.Rep.2013, 3, 3383; [12] Q. Li. *et al.* J. PS 110 (2002) 1-10; [13] Y. Nakayama *et al.* Phys.Chem.Chem.Phys., 2015, 17, 5758; [14] S. Liu *et al.* Eng. Env. Sci., 2012, 5, 9743; [15] N. Jayaprakash *et al.,* Chem.Com., 2011, 47, 12610 ff*;* [16] G. M. Brown, *US 2012/0082904 A1*; [17] C. M. Julien *et al.*, Inorg. 2014, 2, 132-154;