DECHEMA FORSCHUNGSINSTITUT

Transport properties of EMIMCl:$AlCl_3$ mixtures for the Al-ion battery

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Funded by: EU H2020
Period: 01.06.2015 - 31.05.2019

Introduction

The development of Aluminium-ion or Aluminium-metal battery, a post Lithium-ion battery technology, has been hindered in the past decades by the absence of a suitable electrolyte for reversible aluminium deposition and dissolution. Recently, Endres et al. as well as Abbott et al. provided promising results on the reversible plating of aluminium in Ionic Liquid (IL) based electrolytes. [1-4]

Table 1 – Electrolyte mixtures suitable for aluminium metal deposition and dissolution

Solvent	Salt	Ratio	Anion	Cation	Active species	Lit.
EMIMCl	$AlCl_3$	1:1.25	$AlCl_4^-$ / $Al_2Cl_7^-$	$EMIM^+$	$Al_2Cl_7^-$	1,2
EMIMCl	$AlCl_3$	1.1.5	$Al_2Cl_7^-$	$EMIM^+$	$Al_2Cl_7^-$	1,2
Urea	$AlCl_3$	1:1	$AlCl_4^-$	$[AlCl_2 \cdot CH_4N_2O^+]$	$[AlCl_2 \cdot CH_4N_2O^+]$	3,4
Acetamide	$AlCl_3$	1:1	$AlCl_4^-$	$[AlCl_2 \cdot nAmide]^+$	$[AlCl_2 \cdot nAmide]^+$	3,4

Different imidazolium ILs, e. g. EMIMCl (Ethyl-methyl-imidazolium chloride), as well as amide-based compounds were found to be active when combined with $AlCl_3$. IL/$AlCl_3$ mixtures are highly sensitive to water and air, whereas amide/$AlCl_3$ mixtures seem to be less sensitive. [2,4]

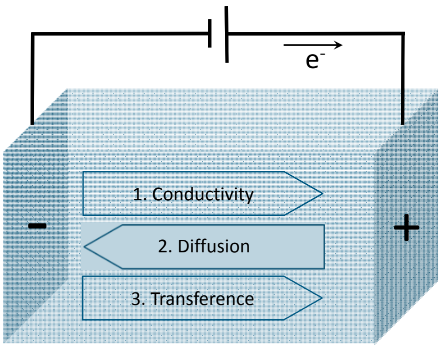


Fig. 1 – Cation transport in the electrolyte when voltage is applied

Aluminium ion transport

Ion transport properties, e. g. ionic conductivity, diffusion and transference influence overall activity of the battery. Most ILs have a high viscosity that may result in low ionic conductivity and diffusion and thus affect battery performance. In ALION project, DFI will provide experimental parameter for a 1D Al-ion cell model to partner TU Berlin.

In contrast to conventional aqueous electrolytes, preparation of ideal diluted solutions of water sensitive IL mixtures such as EMIMCl:$AlCl_3$ is not possible, so that strong ion/ion interactions and presence of e.g. $Al_2Cl_7^-$ and/or $AlCl_4^-$ influence ion mobility. Thus, measurement and data evaluation techniques in highly concentrated mixtures are not trivial and are still controversially discussed. [5-11] In this work, electrochemical methods were preferentially used because of their similarity to real cell design and operation.

1. Conductivity / ΔE [6,7]

Driving force: cell voltage
Measurement technique: impedance spectroscopy
Electrodes: blocking (Graphite, GC, Pt, etc.)
Measurement range: 1 Hz-1 MHz / AC amplitude: 10 mV

2. Diffusion / Δc [8,9]

Driving force: concentration gradient
Measurement technique: potentiostatic polarization+EIS
Electrode: non blocking: aluminium
Measurement range: DC potential: 10mV + EIS: 1 Hz-1 MHz / 10 mV (AC)

3. Transference / ΔE [9-11]

Driving force: cell voltage
Measurement technique: 1) potentiostatic polarization + EIS or 2) very low frequency EIS
Electrode: non blocking: aluminium
Measurement range: 1) DC potential: 10mV + EIS: 1 Hz-1 MHz / 10mV (AC)
2) vlf-EIS: 0.1mHz-1MHz; 1 mV (AC)

Fig. 2 – Different ion transport measurement techniques used in this work

The measurement setup

Test cells:

- Cell body: PEEK or PTFE (Fig. 3 A,B)
- Electrodes: stainless steel, Ø = 12 mm
- Interspace: manually adjusted, 100 µm +/- 10 µm
- T-Cell assembled and sealed under inert conditions (O_2 and H_2O < 0.1 ppm)

Test chamber:

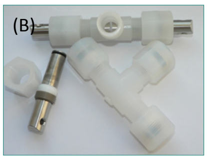
- Heating chamber: Shimadzu GC-14B
- Temperature accuracy: +/- 0.02 °C
- Temperature range: 10 – 75 °C
- Impedance measurements: Zahner IM6ex
- Further measurements: Ametek PMC1000

Thermal expansion problem:

- Irreversible interspace change: > 50 %
- Cause: dilation of all cell components due to increasing temperature

Solution:

- Interspace adjustment with different size PEEK sleeves as spacers (Fig. 3 C)



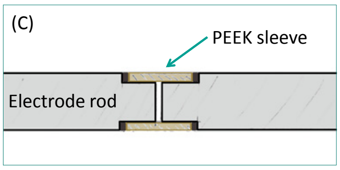


Fig. 3 – (A) T-Cell with adjustable electrode distance; (B) T-Cell assembly; (C) modified cell with PEEK sleeve.

Conductivity data on EMIMCl:$AlCl_3$

Potentiostatic impedance measurements were performed in a 2-electrode setup:

- **Cell constant** determination using a KCl standard solution
- **Impedance measurements** with different EMIMCl:$AlCl_3$ mixtures
- **Ohmic resistance evaluation** at point of lowest phase angle (~ 10^5 Hz)

An exemplary measurement graph (Fig.4.) is depicted, as well as first results in table 2.

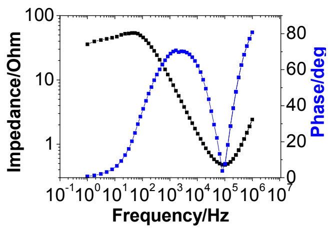


Fig. 4 – Exemplary bode plot

Table 2 – First results on conductivity of EMIMCl:$AlCl_3$ mixtures and literature data.

Solvent: Salt	Molar Ratio	Temperature °C	Resistance Ω	Conductivity mS/cm	Literature data mS/cm
EMIMCl:$AlCl_3$	1:1	25	-	-	23.0 [12] / 18.7 [13]
EMIMCl:$AlCl_3$	1:1.25	24.12	1.08	27.8	-
EMIMCl:$AlCl_3$	1:1.5	25.02	1.91	15.6	15.0 [12]

Conductivity of IL mixture increases with decreasing $AlCl_3$ as expected.

Resume and outlook

In the first project period, a special cell has been designed for evaluation of ionic conductivity, diffusion coefficient and transference number of EMIMCl:$AlCl_3$ mixtures at different temperatures (10-60°C). First conductivity results obtained for EMIMCl:$AlCl_3$ 1:1.5 mixture are in agreement with literature. Temperature dependency of ion conductivity will be measured with the modified cell assembly. Measurement of diffusion coefficient and transference number will proceed accordingly.

Acknowledgements

The European Commission is gratefully acknowledged for financial support within the research and innovation program Horizon 2020. (Grant No.: 646286 – ALION)

[1] S.Z. El Abedin et al., EC Com. 12 (2010) 1084-1086; [2] S. Z. El Abedin, Electrochem. Commun., 7 (2005) 1111-1116; [3] H. M. A. Abood, Chem. Commun., 47 (2011) 3523-3525; [4] A. P. Abbott, Phys. Chem. Chem. Phys., 16 (2104) 14675; [5] R. Tao et al., Journal of Power Sourches 135 (2004) 267-272; [6] H. A. Every et al., Phys. Chem. Chem. Physl, 2004, 6, 1758; [7] M. Zistler et al., Electrochemica Acta 52 (2006) 161; [8] M. Zistler, Dissertation 2008, Universität Regensburg; [9] S. Zugmann et al., ElectrochemicaActa 56 (2011) 3926; [10] M. Amereller et al., Progress in Solid State Chemistry 42 (2014) 39; [11] M. M. Hiller et al., ElectrochimicaActa 114 (2013) 21; [12] P. Wasserscheid, Ionic liquids in synthesis, Wiley VCH, 2008; [13] R. L. Perry, J. of Chem. and Eng. Data 40, (1995) 615.