ARTICLE

## Supplementary Information

# Investigation of $Al(TfO)_3$ based deep eutectic solvent electrolytes for aluminium-ion battery. Part I: Understanding positive Al complex formation†

Willi Peters,[a] Huong Thu Duong,[a] Soobin Lee[a] and Jean-Francois Drillet[a,]*

[a] DECHEMA Research Institute, Batteries & Fuel Cells, 60486 Frankfurt am Main, Germany; * E-mail: jean.drillet@dechema.de

## Physical properties of electrolyte components:

Table S1 – Physical properties of all electrolyte components; * solid at room temperature; ** decomposition temperature; *** 70% urea mixture with water. The following literature has been used: (a) Merck, Safety data sheet CAS:607-194-00-1; (b) E. AVCI: J. Inno Sci Eng 1 (2017) 25; (c) S. C. DeVito et al.,Encyclopedia of Chemical Technology. (1999-2014). John Wiley & Sons; (d, f) J. A. Riddich et al. Techniques of Chemistry 4, 2 (1985), 658; (e) S. Halonen et al. Emiss. Control Sci. Technol. 3, (2017), 161-170

| **Used electrolyte components** (incl. abbreviations) | **Molar Mass** $g\ mol^{-1}$ | **Melting point** °C | **Boiling point** °C | **Viscosity at 20 °C** mPas |
|---|---|---|---|---|
| **Propylene carbonate (PC)** | 102.09 | - 48.8 | 242 | 2.51 (@25 °C) (a) |
| **Formamide (FA)** | 45.04 | 2 | 210 | 3.75 (b) |
| **Acetonitrile (ACN)** | 41.05 | - 45 | 82 | 0.36 (c) |
| **N-Methylacetamide (NMA or N)** | 73.09 | 27 - 30 | 206 - 208 | 3.01 (@ 40°C)* (d) |
| **Urea (U)** | 60.06 | 133 ** | 133 ** | 1.23 (@80°C)*** (e) |
| **Acetamide (AcAm or A)** | 59.07 | 65 - 81 | 222 ** | 2.182 (@91.1°C) * (f) |
| **Aluminiumtrifluoromethanesulfonate ($Al(TfO)_3$ or AT)** | 474.19 | 300 | - | - |

## Water content determination via volumetric Karl-Fischer titration:

Table S2 – Water content determination of single components and $Al(TfO)_3$-free mixtures via Karl-Fischer-Titration; * Component dried with molecular sieve

| **Components** (incl. abbreviations) | **Composition** % | **Measured water content** ppm | % |
|---|---|---|---|
| **NMA*** | | 101 | 0.010 |
| **FA*** | | 29 | 0.003 |
| **PC *** | | 19 | 0.002 |
| | | | |
| **NMA* / Urea** | | 999 | 0.100 |
| **NMA* / Urea*** | | 25 | 0.002 |
| **NMA*/AcAm** | | 1412 | 0.141 |
| **NMA*/AcAm*** | | 113 | 0.011 |
| **FA* /Urea*** | | 255 | 0.025 |

All solvents were dried down to 100 ppm and below by using a molecular sieve. Drying of the hygroscopic urea and acetamide with a molecular sieve reduced water amount significantly from 999 to 25 ppm and from 1412 to 113 ppm, respectively. Volumetric KFT technique is, however, unsuitable for mixtures containing $Al(TfO)_3$ salt since the latter reacts with the titration substance iodine.

 

## Full Raman spectrum:

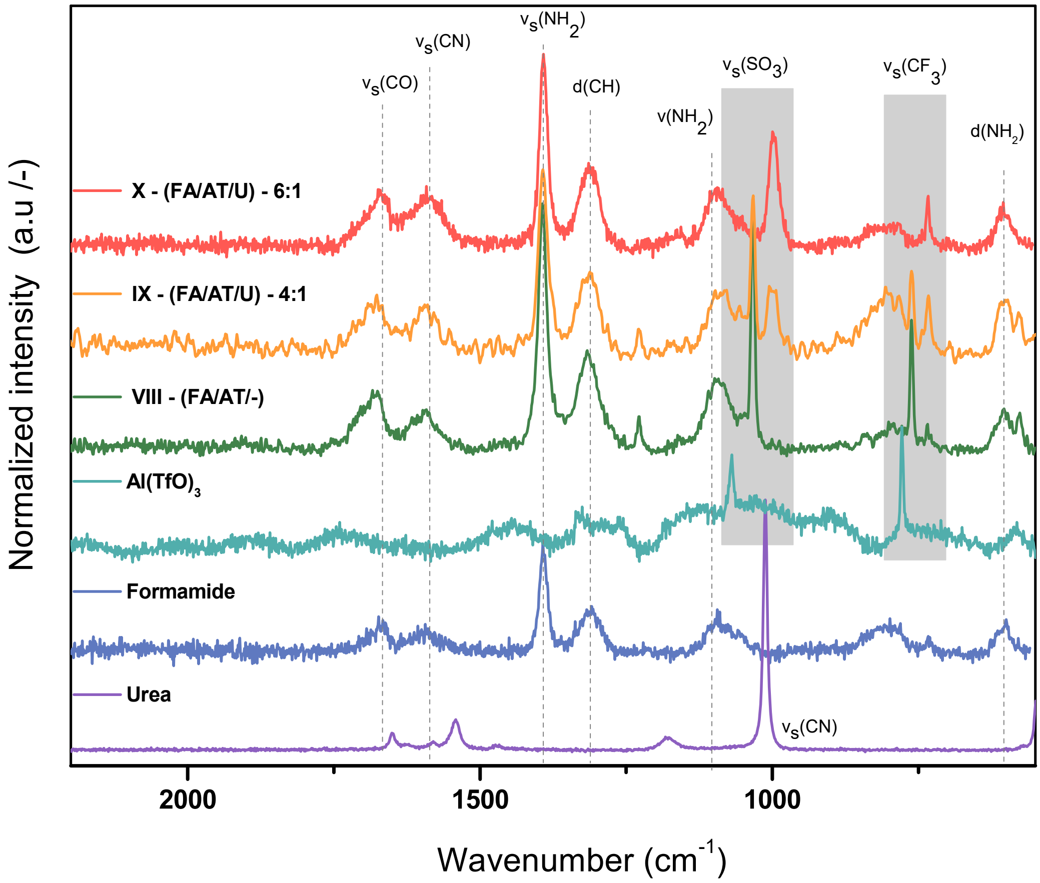


Figure S1 – Raman spectra of all FA-based single components as well as binary and ternary mixtures corresponding to Fig. 5b with an increased measurement range from 100 to 2400 $cm^{-1}$

## Raman measurement summary: TfO peak positions

Table S3 – Summary of $SO_3$ and $CF_3$ peak positions for single. binary and ternary electrolyte mixtures determined via Raman spectroscopy; Prominent peaks intensity are printed in bold; [a]ACN and PC are partially immiscible with urea – inhomogeneous mixtures were measured nonetheless; [b]mixture with urea/AT ratio of 6:1. all other ternary mixtures were measured at a ratio of 4:1; Peak position is correlated to single-charged **(*)** or twofold-charged **(#)** positive Al-ion complex.

| | | **$SO_3$** $cm^{-1}$ | | | | **$CF_3$** $cm^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| | | solid | (#) | (*) | (#) | solid | (*) | (#) |
| - | Al(TfO)$_3$ | **1070** | - | - | - | **778** | - | - |
| **VII** | NMA / Al(TfO)$_3$ | - | - | **1032** | - | - | **761** | - |
| **V** | NMA / Al(TfO)$_3$ / Urea | - | 1041 | **1032** | - | - | 761 | **732** |
| **I** | NMA / Al(TfO)$_3$ / AcAm | - | - | **1032** | - | - | 761 | |
| **VIII** | FA / Al(TfO)$_3$ | - | - | **1032** | - | - | **761** | 734 |
| **IX** | FA / Al(TfO)$_3$ / Urea | - | - | **1032** | 999 | - | **761** | 734 |
| **X** | FA / Al(TfO)$_3$ / Urea [b] | - | - | - | 999 | - | - | **734** |
| **XI** | ACN / Al(TfO)$_3$ | - | - | - | - | - | - | **734** |
| - | ACN / Al(TfO)$_3$ / Urea [a] | - | - | 1032 | - | - | **761** | 734 |
| **XII** | PC / Al(TfO)$_3$ | - | - | **1032** | - | - | **761** | - |
| - | PC / Al(TfO)$_3$ / Urea [a] | - | - | **1032** | - | - | **761** | - |

The comparison of $CF_3$ and $SO_3$ peaks in the Raman spectra shows a clear trend to lower wave numbers for all measured electrolytes.

## Raman spectra of NMA/AcAm mixtures with $Al(NO_3)_3$ or $Al(TfO)_3$ salt:

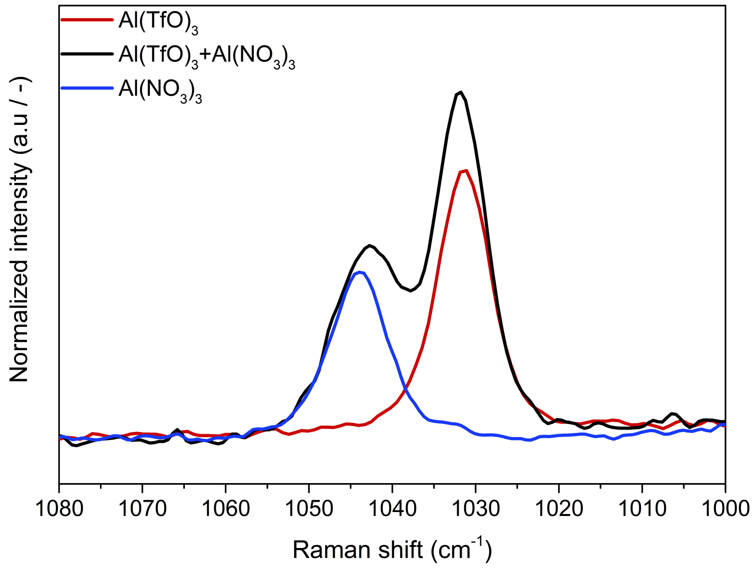


Figure S2 – Raman spectra of electrolytes containing $Al(TfO)_3$ a/o $Al(NO_3)_3$: Black: NMA/$Al(TfO)_3$/$Al(NO_3)_3$/AcAm; Red: NMA/$Al(TfO)_3$/AcAm; Blue: NMA/$Al(TfO)_3$/AcAm

Nitrate containing DES depicts a clear peak at higher wave numbers, due to their stronger association to the Al-ion. This is supported by NMR data, where an aqueous $Al(NO_3)_3$ solution was used as reference.

## Temperature dependence of binary and ternary electrolytes:

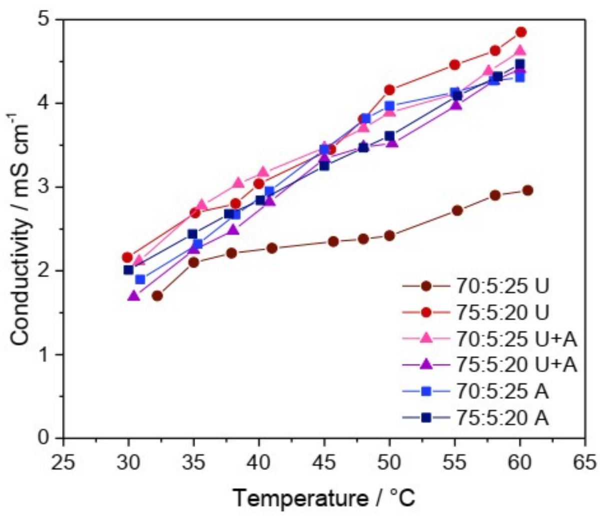


Figure S3 – Conductivity of DES based on HBD type and content