Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

Supporting Information for Publication

Glyme-based liquid-solid electrolytes

for lithium metal batteries

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Content:

- Optical images of dry AAO membranes and liquid-solid electrolytes
- Infrared spectroscopy and viscosity of liquid LiTf/triglyme electrolytes
- Calculation on the number of saturation concentration in AAO-based liquid-solid electrolytes
- Details on galvanostatic polarization experiments of liquid and liquid-solid electrolytes
- Determination of the SEI thickness on lithium electrodes based on impedance

spectroscopy

Optical images of dry AAO membranes



Figure S1. Photo showing AAO: (1 M LiTf/triglyme) liquid-solid electrolyte (left) and dry AAO membrane (right).

Infrared spectroscopy and viscosity of liquid LiTf/triglyme electrolytes

In Figure S2, the triflate stretching band in IR spectra of 1M LiTf : triglyme at 25°C (A) and 80° C (B) are illustrated. Three local maximum in the range of 745-770 cm⁻¹ are assigned to free ions (757 cm⁻¹), ion pair (752 cm⁻¹) and bigger aggregates such as dimers (761 cm⁻¹).¹ As it can be observed in Figure S2, c upon increasing the temperature the concentration of free ions decreases while concentration of pair and dimers are increasing.



Figure S2. Infrared spectra of the triflate stretching band for 1 vol% AAO: (1 M LiTf/triglyme) at a) room temperature, b) 80 °C. Concentration of the free ions (green), ion pairs (pink) and dimers (yellow) has been determined from the Gaussian fit (dashed red line) of the total measured spectra (continuous blue line), c) Temperature dependent concentrations of free ions, ion pairs and dimers.



Figure S3. Temperature dependence of viscosity for liquid 1 M LiTf/triglyme.

Calculation of the saturation concentration in AAO-based liquid-solid electrolytes

AAO pellet contains pores with conical frustum form. Accordingly, the surface of one pore can be determined from:

$$A_{pore} = \pi (R+r) \sqrt{(R-r)^2 + h^2}$$
, Eq. 1

where *R* is the radius of the bigger pore side, *r* is the radius of the smaller pore side and *h* is the height of the pore. The surface area can be calculated from:

$$Surface area = \frac{A_{pore} \times N_{pore}}{m_{pellet}}, \qquad Eq. 2$$

where N_{pores} is the number of pores, and m_{pellet} ist the mass of one dry AAO pellet. Total surface area is on the other hand:

$$A_{total} = Surface \ area \ \times \ m_{Pellet},$$
 Eq. 3

while the number of -OH groups can be taken as

$$N_{OH} = 6 * A_{total}.$$
 Eq. 4

The number of available lithium ions (when completely dissociated) is

$$N_{Li+} = N_A C_{salt} \frac{m_{liquid}}{d_{liquid}},$$
 Eq. 5

where m_{liquid} is the mass of infiltrated liquid electrolyte ($m_{\text{liquid}} = m_{\text{composite}} - m_{\text{pellet}}$), and d_{liquid} is the density of liquid electrolyte. Finally, the saturation concentration is calculated from the ratio:

$$C_{salt} = \frac{N_{OH}}{N_{Li+}}$$
 Eq. 6

Details on galvanostatic polarization experiments of liquid and liquid-solid electrolytes



Figure S4. Galvanostatic polarization curve for 1 M LiTf/triglyme. The steady state is reached after quite a long time, b) Impedance spectra before (black) and after (red) galvanostatic polarization. Observed semicircle corresponds to the SEI resistance, changing during the polarization. The measured lithium transference number is 0.15.



Figure S5. Galvanostatic polarization of 1-Methyl-1-Propylpiperidinium bis(trifluoromethylsulfonyl)imide ionic liquid containing 0.2 M LiTf. The measured lithium transference number is 0.006.



Figure S6. Galvanostatic polarization of AAO:1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide ionic liquid containing 0.2 M LiTf. The measured lithium transference number is 0.03.



Figure S7. Temperature dependent galvanostatic polarization of AAO: (1 M LiTf/triglyme).



Figure S8. Extraction of the salt diffusion coefficient from the long polarization times for a) 10°C, b) 80°C.



Figure S9. Galvanostatic polarization of a) AAO: (0.02 M LiTf/triglyme), b) AAO: (2 M LiTf/triglyme).



Figure S10. Extraction of salt diffusion coefficients from the long polarization times for a) AAO: (0.02 M LiTf/triglyme), b) AAO: (2 M LiTf/triglyme).

Determination of the SEI thickness on lithium electrodes based on impedance spectroscopy

Plotting the negative imaginary part (Z'') versus the real part (Z'') of the impedance gives the Nyquist diagram that can be evaluated by fitting it to an appropriate equivalent circuit. The equivalent circuit includes capacitances and resistors to describe the electrochemical behaviour. In the simplest case where there is just the bulk response this equivalent circuit consists of a resistor parallel to a capacitor (*RC*). The complex impedance of this single *RC* parallel circuit is:

$$Z^* = \frac{R}{1 + i\omega R}$$
 Eq. 7

The Nyquist plot of *RC* element appears as a semicircle with a radius of $(\overline{2})$. The relaxation time (τ) of each process corresponding to the semicircle can be derived using the frequency at the maximum of the semicircle:

$$\tau = \omega_{max}^{-1}$$

However, in a real system normally processes such as interfacial layers or grain boundaries are involved which can appear as multiple contributions to impedance spectra depending on the relaxation times. In such cases, the impedance spectra can be fitted using several *RC* elements in series.

The ionic conductivity of the bulk (σ_{Bulk}) can be calculated using the fitted resistance (R_{Bulk}) obtained from diameter of the arc:

$$\sigma_{Bulk} = \frac{L}{R_{Bulk}A}$$
 Eq. 9

with L and A representing thickness and area of electrode, respectively.

Bulk capacitances (C_{Bulk}) can be derived from the maximum frequency (ω_{Max}) :

$$\omega_{Max} = (R_{Bulk} C_{Bulk})^{-1}$$
 Eq. 10

However, the semicircles are usually depressed due to inhomogeneity or porosity, and in these cases, it is possible to calculate the true capacitances (${}^{C}{}^{Tr}_{Bulk}$), taking into account the elements of the equivalent circuit according to:

$$c_{Bulk}^{Tr} = (C_{Bulk}^{1-\alpha}Q_{Bulk})^{1/\alpha}$$
Eq. 11

where α and Q are parameters (CPE-P and CPE-T) from the corresponding fit of the semicircle. Additionally, C_{Bulk} is related to the electrodes area (A) and the distance between the electrodes d_{Bulk} via:

$$C_{Bulk} = \varepsilon_0 \varepsilon_{Bulk} \frac{A}{d_{Bulk}}$$
 Eq. 12

where (ε_{Bulk}) is the dielectric constant of the medium. Similar relations are valid for interlayers such as SEI. Hence the thickness of the interfacial layer (d_{SEI}) can be calculated from the capacitances ratio with the assumption that the dielectric constants of SEI and bulk are identical:

$$\frac{C_{SEI}}{C_{Bulk}} = \frac{d_{Bulk} \varepsilon_{SEI}}{d_{SEI} \varepsilon_{Bul}} \approx \frac{d_{Bulk}}{d_{SEI}}$$
Eq. 13

The spectra have been analysed using the ZView software. Figure S11 shows the typical recorded impedance spectra and fitted equivalent circuit in this study.



Figure S11. Typical impedance spectra recorded in the Li|AAO: (LiTf/triglyme)|Li cell and the corresponding fitted equivalent circuit.