

# In-operando evaluation of selectivity and transference number of lithium conductive membranes

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**Abstract:** Lithium selective membranes are important to prevent undesirable effects of electrodes' cross-talk in Li-S and Li-O<sub>2</sub> cells, such as crossover of redox species from the cathode to the anode. This work reports a novel approach to evaluate their selectivity in-operando, under practically relevant conditions, including application of a current through the membrane. The method is illustrated with a lithiated Nafion membrane, immersed in 1 molal LiTFSI in diglyme containing 0.1 molal I<sup>-</sup> as a model crossover species, and an accurate evaluation of the transference number of crossover species is reported ( $t_{I^-} = 0.0126 \pm 0.0018$ ). It is also shown that the standard ex-situ methods of evaluation of membrane selectivity, as applied without a current passing through the membrane, provide a considerable overestimation of the capability of the membrane to block crossover species.

## Introduction

Lithium selective membranes have the potential to revolutionize the performance of lithium batteries. Promising post Li-ion candidates such as Li-S and Li-O<sub>2</sub> batteries operate with polysulfides or redox mediators that facilitate the reactions at the positive electrode, but those species are unstable at the lithium electrode, and hence protective lithium selective membranes or coatings are required<sup>[1-6]</sup>. For these applications, a key property is the ability of the membrane to conduct lithium ions and block any other species. Furthermore, membranes able to transport only lithium ions (thus, with a unity lithium transference number) are highly advantageous since they overcome the problem of formation of concentration gradients during the operation of the cell, which would induce lithium dendrite formation<sup>[7]</sup>. A number of promising single lithium-ion conducting polymers have been developed<sup>[8]</sup> and this work proposes a new method to quantify their selectivity and transference number that overcomes some of the assumptions of previous methods.

The selectivity of membranes has traditionally been evaluated ex-situ using an H-type cell configuration comprising two high-volume electrolyte compartments with the membrane clamped in between<sup>[9-10]</sup>. Test crossover species are introduced in only one of the electrolyte compartments, and the increase in concentration in the other compartment is monitored over time.

We recently developed a new approach in which the rate of transport of crossover species through membranes was determined in-situ using a modified Swagelok cell incorporating a glassy carbon electrode as an electrochemical sensor to detect crossover species, which allowed an unprecedented sensitivity and reproducibility, as well as operation under realistic cell conditions (e.g. use of minimum amount of electrolyte)<sup>[11]</sup>.

However, membranes are used in cells in which a current has to be applied. Thus in this work, we have developed a cell set-up that allows the characterization of the rate of transport of crossover species through membranes as a function of the applied current. It is shown that application of a current can produce a marked increase in the rate of crossover of species, thus demonstrating that the selectivity of the membrane can be overestimated by performing the experiments ex-situ without application of a current.

The selectivity of the membrane can also be inferred from the measurement of the lithium transport number, which can be obtained via potentiostatic or galvanostatic polarization of a cell containing the membrane sandwiched between two lithium electrodes<sup>[12-14]</sup>. Unfortunately, this method is not applicable for membranes that react in contact with lithium, and for membranes in contact with a liquid electrolyte compartment, the absence of convection effects, as required by the Bruce-Vincent analysis, is difficult to be fulfilled<sup>[15-17]</sup>.

In this work, we demonstrate a new in-situ method to characterize the rate of transport of redox crossover species across membranes that is applicable to the situation where the membrane is separating two liquid electrolyte compartments. Such hybrid electrolyte cell design combines the advantages of liquid electrolytes, in terms of efficient wetting of the electrode and fast kinetics of the electrochemical reactions, as well as the protective role of lithium selective membranes in the suppression of transport of crossover species<sup>[4, 18-31]</sup>. The method here developed allows the direct measurement of the rate of transport and the transference number of redox crossover species under in-operando conditions (that is, in the presence of an applied current). The method is illustrated here for the case of a lithiated Nafion membrane and its capability to block the transport of iodide ions. Nafion membranes have been successfully used in Li-S cells to block transport of polysulfide species<sup>[22-23, 28, 31-48]</sup>. Iodide has a well-defined redox behaviour<sup>[49]</sup> and it is used here as a model for polysulfide redox species, which will be studied in further work. The mathematical analysis (described in section 1 of the Supplementary Information) is derived for the situation under study, in which the rate of transport of redox crossover species within the membrane is much smaller than in the liquid electrolyte compartments. This condition implies that the membrane is more efficient at suppressing the transport of redox crossover species than the liquid electrolyte, which should be the case for lithium protective membranes. But this condition does not require a low conductivity of the membrane, since the rate of transport of lithium ions within the membrane could be very high.

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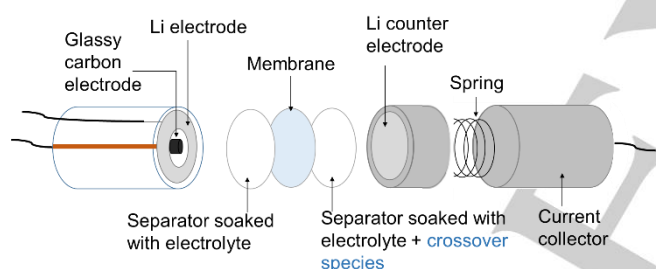
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## Results and Discussion

Figure 1 shows a sketch of our cell set-up, which includes a glassy-carbon electrochemical sensor to detect the crossover species (iodide in this case) as they travel from one liquid electrolyte compartment (which we call counter electrode compartment), through the membrane (in this case, Celgard coated with lithiated Nafion), to the liquid electrolyte compartment in contact with the glassy carbon sensor (which we call working electrode compartment). The cell also includes two lithium electrodes, one at each side of the membrane, to pass current. The liquid electrolyte compartments are glass fibre separators impregnated with 1 molal LiTFSI in diglyme, with 0.1 molal (0.0939 molar) LiI present initially in the counter electrode compartment only. Cyclic voltammetry is used to quantify the I<sup>-</sup> concentration in the glassy carbon electrode compartment over time (see Section 2 in the Supplementary Information for details on the calibration of values of peak current to extract concentration values).

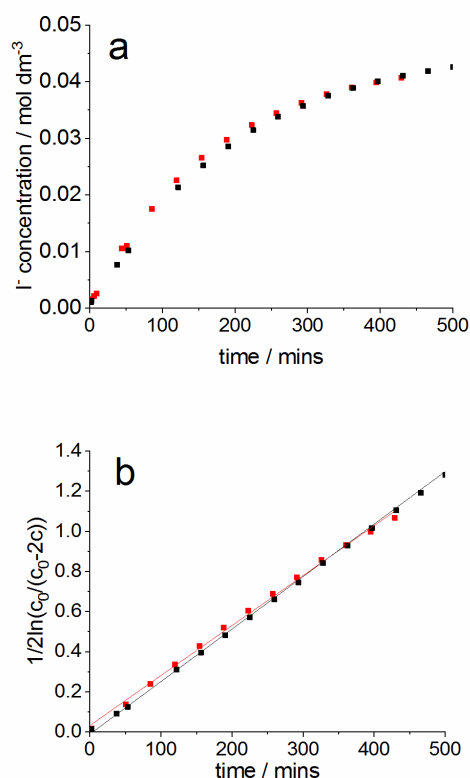
Figure 2a shows the evolution of the I<sup>-</sup> concentration with time under open circuit conditions (that is, without the application of a current through the membrane). It is observed that at long times, the I<sup>-</sup> concentration slowly approaches 0.047 molar, which is half the concentration initially present in the counter electrode compartment.



**Figure 1.** Sketch of the cell set-up.

The results can be analysed with a simple model that considers that the rate of transport of crossover species through the membrane is much slower than in the liquid electrolyte compartments (full derivation is provided in the Supplementary Information, Section 1). Additional experiments using an uncoated separator, instead of the Nafion-coated membrane (Figure S7), confirm that the rate of crossover is much faster in the electrolyte-filled separator. According to this model, the variation of concentration over time is given by:

$$c = \frac{1}{2} c^* \left( 1 - \exp \left[ \frac{2\tau_1 - 2t}{\tau_2} \right] \right) \quad \text{Eq.1}$$



**Figure 2.** (a) Increase over time in the concentration of iodide in the working electrode compartment of a two-compartment cell, as described in Fig. 1, initially containing 0.1 m LiI in the counter electrode compartment only, under open circuit conditions. The compartments are separated by a Celgard membrane coated on both sides by lithiated Nafion. The plot shows results from repeat experiments obtained with two different cells. (b) Data shown in (a), replotted using Equation 3.

where  $c$  is the concentration of crossover species at the glassy carbon electrode compartment,  $c^*$  is the initial concentration of crossover species at the other electrolyte compartment (which we call counter electrode compartment),  $t$  is time,  $\tau_1$  is the time required to reach a linear variation of concentration with distance through the membrane and  $\tau_2$  is given by:

$$\tau_2 = \frac{L_m L_l}{P_m} \quad \text{Eq.2}$$

where  $P_m$  is the permeability coefficient of the crossover species through the membrane, and  $L_m$  and  $L_l$  are the thicknesses of the membrane and the liquid electrolyte compartments, respectively (when compressed in the cell). Re-arrangement of equation 1 gives:

$$\frac{1}{2} \ln \left( \frac{c^*}{c^* - 2c} \right) = \frac{t - \tau_1}{\tau_2} \quad \text{Eq.3}$$

and Figure 2b shows that the plot of  $1/2 \ln(c^*/(c^* - 2c))$  vs.  $t$  is indeed linear. The inverse of the slope of the fit gives a value of  $\tau_2 = 389 \pm 10$  minutes, from which, using equation 2, the

value of the permeability coefficient is evaluated as  $P_m = (2.7 \pm 0.4) \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  (where error bars are obtained from the reproducibility of the experiments). The permeability coefficient is also called diffusive permeability or simply permeability, and the present results are in reasonable agreement with previous studies of lithiated Nafion membranes in non-aqueous electrolytes<sup>[50-51]</sup>.

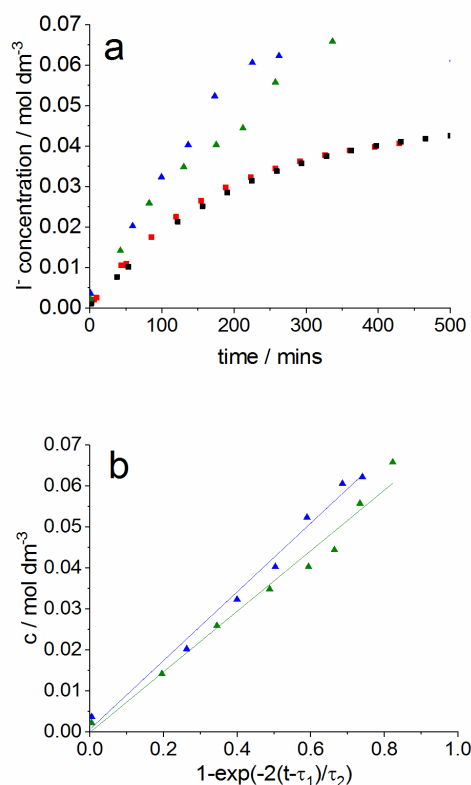
Figure 3a shows that faster rates of crossover are observed in the presence of an applied current, thus evidencing that the selectivity of the membrane can be overestimated if the measurements are done ex-situ without the application of a current. Figure 3b shows that the plot of  $c$  vs.  $(1 - \exp[-(2\tau_1 - 2t)/\tau_2])$  is linear, as expected from the model. From the slope of the fit, using equation 4, the  $\text{I}^-$  transference number is estimated as  $t_{\text{I}^-} = 0.0126 \pm 0.0018$ . The very low value of the  $\text{I}^-$  transference number found here implies a very high selectivity of the membrane towards  $\text{Li}^+$ . It is worth mentioning that this evaluation of the transference number is based on the fit of experimental data, with and without current, and it only requires input of experimental parameters that are well-known, specifically, the thickness of the liquid electrolyte compartments and the initial concentration of redox crossover species at the counter electrode compartment. Full details of the calculations are given in the supplementary information, at the end of section 1.

The value of  $0.0126 \pm 0.0018$  for the  $\text{I}^-$  transference number obtained from the experiments under application of current can be compared with an approximate estimation of the transference number obtained by combining the results of the permeability coefficient,  $P_m$ , and the conductivity of the membrane,  $\sigma_m$  (see details in the Supplementary Information, Section 5), which is derived using the Nernst-Einstein equation. This gives a value of the transference number of  $t_{\text{I}^-} = 0.013 \pm 0.004$ , which is in excellent agreement, but it should be noted that the Nernst-Einstein equation is not expected to be applicable in the presence of ion-ion interactions. The properties of the membrane employed here are not expected to be the same as other lithiated Nafion membranes, but it is also worth mentioning that, by combining reported values of the  $\text{I}^-$  permeability coefficient and membrane conductivity reported in other studies<sup>[50]</sup>, consistent values of the  $\text{I}^-$  transference number are obtained.

## Conclusions

In conclusion, we have developed a new approach that allows the accurate evaluation of the selectivity of lithium conductive membranes in contact with liquid electrolytes under in-operando conditions, that is, while those membranes are used in hybrid cells under application of a current. It is shown that the membrane selectivity can be overestimated if the measurements are restricted to ex-situ conditions where application of a current is not possible. A simple mathematical model is developed to describe the data here presented, in which the rate of transport of redox crossover species within the membrane is much slower

than inside the liquid electrolyte. It is shown that this approach also allows an accurate evaluation of the transference number of redox crossover species, which is obtained from the fit of experimental data with and without current and only requires input from well-known experimental parameters.



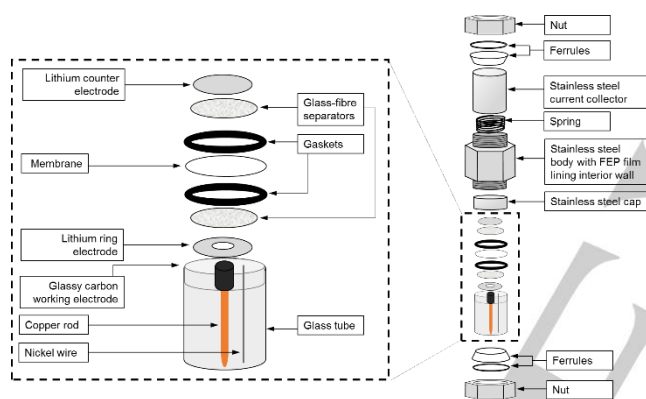
**Figure 3.** (a) Increase over time in the concentration of iodide in the working electrode compartment of a two-compartment cell, under open circuit conditions (squares, data of Figure 2a) and on application of current of 1 mA cm<sup>2</sup> (triangles). The plot shows results from repeat experiments obtained with two different cells for each condition. (b) Data shown in (a), replotted using equation 3.

## Experimental Section

Figure 4 shows the details of our cell design. As in our previous work<sup>[11]</sup>, a glassy carbon working electrode or 'probe' (3 mm diameter, type 2, Alfa Aesar) is embedded in a 1-inch diameter borosilicate glass disc attached to a glass tube which fits a standard 1 inch 'Swagelok' cell. A thin copper rod in contact with the back face of the glassy carbon serves as the current collector. In the design presented in this work, a further ring-shaped lithium electrode can now be placed on the same side as the glassy carbon probe, with a nickel wire embedded in the glass disc approximately 5 mm from the edge of the glassy carbon serving as the current collector. The additional electrode allows  $\text{Li}^+$  ions to be passed through the membrane by applying a constant current between this electrode and a lithium counter electrode on the opposite side. This current can be periodically interrupted to allow recording of voltammograms at the glassy carbon electrode at intervals in time.

Chemically resistant gaskets (Ekraz 9655B, 24.5 mm outer diameter x 18.5 mm inner diameter x 0.5 mm thickness, supplied by Polymax Ltd.), coated with a thin layer of vacuum grease (Dow-Corning high vacuum silicone grease), prevent leakage of electrolyte around the edge of the membrane.

LITHion™ dispersion (10–12 wt% in isopropyl alcohol, Ion Power) was mixed in the ratio 1:1 with additional isopropyl alcohol (>=99.5%, Fisher). Lithium-selective membranes were prepared by drop-coating this mixture onto both sides of a Celgard separator (Celgard 2320). Celgard sheets, ca. 40 x 40 mm, were clamped in a flat position and 110  $\mu\text{L}$  of the LITHion mixture was drop-coated onto a central circular area, ca. 28 mm diameter, on one side of the sheet. This side was allowed to air-dry and the process was repeated for the other side, giving a dry mass loading of ca. 1 mg  $\text{cm}^{-2}$  on each side. Once air-dry, the coated membranes were punched to 25 mm diameter and further dried under vacuum (unheated) for 72 hours, prior to use. Uncoated Celgard membranes were punched to the same diameter and dried in the same way. The thickness of coated membranes and separators was measured with a thickness gauge (Mitutoyo® ABSOLUTE Digimatic ID-C112X). In the case of glass fibre separators, which are compressible, the thickness of the compressed separator was measured immediately after cell disassembly.



**Figure 4.** Technical details of Swagelok cell modified with glassy carbon probe and two electrodes (a lithium disc and a ring) to allow measurements of the rate of crossover of species across membranes as a function of the applied current between the two lithium electrodes.

Glass fibre separators (Whatman GF-F, punched to 14 mm diameter) were dried under vacuum at 120 °C for 24 hours. Prior to each use, glassy carbon electrodes were polished in deionised water (Purite, 18.2 M $\Omega$  cm) with 25, 3.0 and 0.3  $\mu\text{m}$  alumina powder and finally on a 'blank' polishing pad, and then rinsed in deionised water. They were then dried, along with other cell components, under vacuum at 80 °C for a minimum of 1 hour before being transferred to an argon filled-glovebox (<1 ppm water content, < 10 ppm oxygen content, mBraun) and allowed to cool.

For the electrolytes, lithium bis(trifluoromethane)-sulfonamide salt (LiTFSI) (99.95%, Sigma-Aldrich) and lithium iodide (LiI) (anhydrous, 99%, Sigma-Aldrich) were dried and deoxygenated under vacuum at 120 °C for 24 hours. Molecular sieves (4 Å beads, 4–8 mesh, Sigma-Aldrich) were dried under vacuum at 200 °C for 2 days and added to diethylene glycol dimethyl ether (diglyme) (anhydrous, 99.5%, Sigma-Aldrich) which was ready for use after 3 days. Electrolytes (1 molar (0.939 molar) LiTFSI in diglyme + 0–0.1 molar (0–0.0939 molar) LiI) were prepared inside the glovebox. Lithium electrode preparation and cell assembly were carried out inside the same glovebox. Lithium electrodes

were punched from lithium foil (battery grade, 100  $\mu\text{m}$  thickness, Rockwood Lithium), to 13 mm outer diameter and, for the ring-shaped electrode, 5 mm inner diameter. When assembling cells, 55  $\mu\text{L}$  of electrolyte was used for each glass fibre separator.

Conductivity measurements were carried out using half-inch Swagelok cells with copper current collectors. Prior to use, copper current collectors were polished in ethanol using 25, 3.0 and 0.3  $\mu\text{m}$  alumina powder, sonicated in ethanol, rinsed in acetone and dried under vacuum, unheated, for 1 hour before being transferred to the glovebox. Other cell components were prepared as above. Cells were assembled containing either (a) 2 x glass fibre separators, (b) 2 x glass fibre separators with an uncoated Celgard membrane in between, or (c) 2 x glass fibre separators with a LITHion-coated Celgard membrane in between (all 12 mm diameter). 47  $\mu\text{L}$  of electrolyte (1 molar LiTFSI in diglyme) was used for each glass fibre separator. Conductivity was evaluated using electrochemical impedance spectroscopy (EIS).

Electrochemical measurements were carried out using Bio-logic VMP2 and VMP3 variable multichannel potentiostat/galvanostat instruments. Cyclic voltammetry scans were carried out at a scan rate of 20 mV  $\text{s}^{-1}$ . During applied-current experiments, a constant current of 0.9 mA was applied (equivalent to 1 mA  $\text{cm}^{-2}$  at the lithium ring electrode). This current was interrupted at approximately 30 minute intervals, whilst voltammograms were recorded at the glassy carbon electrode. (EIS) measurements were carried out at open circuit potential using a frequency range of 1 MHz to 10 Hz and a voltage perturbation amplitude of 10 mV. All measurements were carried out with the cell placed in climatic chamber (Mettler HPP110) at a temperature of 25 °C. Measurements were initiated a maximum of 2 minutes after cells were assembled.

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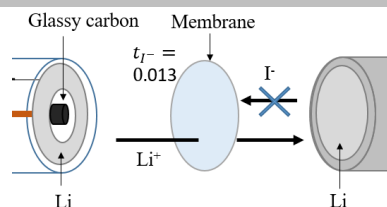
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## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## ARTICLE

We report a novel approach to evaluate the selectivity of lithium-protective membranes, under application of a current through the membrane. The method provides an accurate evaluation of the transference number of redox crossover species, and we show that standard ex-situ methods can considerably overestimate the capability of the membrane to block crossover species.



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