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A simple, fast and accurate in-situ method to measure the rate of transport of redox species through membranes for lithium batteries

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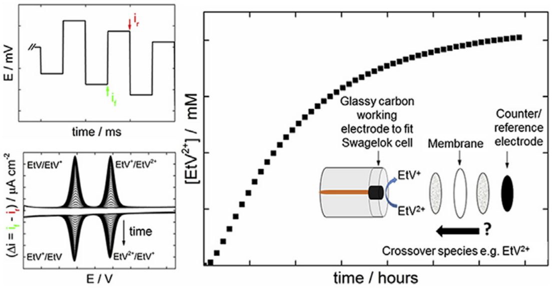
HIGHLIGHTS

- Quantification of crossover of redox species through membranes in lithium batteries.
- Simple, fast, in-situ, quantitative measurements using small electrolyte volume.
- Detection limit of ~10 μM.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium ion conducting membranes are important to protect the lithium metal electrode and act as a barrier to crossover species such as polysulphides in Li-S systems, redox mediators in Li-O_2 cells or dissolved cathode species or electrolyte oxidation products in high voltage Li-ion batteries. We present an in-situ method for measuring permeability of membranes to crossover redox species. The method employs a 'Swagelok' cell design equipped with a glassy carbon working electrode, in which redox species are placed initially in the counter electrode compartment only. Permeability through the membrane, which separates working and counter electrodes, is determined using a square wave voltammetry technique that allows the concentration of crossover redox species to be evaluated over time with very high precision. We test the method using a model and well-behaved electrochemical system to demonstrate its sensitivity, reproducibility and reliability relative to alternative approaches. This new method offers advantages in terms of small electrolyte volume, and simple, fast, quantitative and in-situ measurement.

1. Introduction

Li-S and Li-O_2 battery systems employing a lithium metal negative electrode are attractive due to their high theoretical specific energy. Both systems, however, present a number of challenges [1]. In Li-S systems, shuttling between the positive and negative electrodes of soluble polysulphides gives rise to high rates of self-discharge, lower discharge capacities, incomplete charging, parasitic consumption of the lithium electrode and capacity fade over time [1–8]. The same is true for crossover species in Li-O_2 systems, which may include dissolved oxygen [1,9–11] or electrolyte additives (redox shuttles/mediators) included on the positive electrode side to avoid electrode passivation by the discharge product Li_2O_2 and/or to reduce high overpotentials for oxygen reduction/

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evolution [1,12–32].

The issue of crossover is not confined to Li-S and Li-O_2 systems, however. In lithium-ion batteries, transition metal dissolution from the positive electrode and subsequent deposition on the negative electrode leads to capacity fade [33,34]. Similar effects can arise from unwanted shuttling of electrolyte oxidation products [35].

One approach to tackling these issues is the use of a lithium-ion conducting membrane (LICM) to protect the lithium metal (or other negative) electrode [36–51]. Such a membrane allows passage of lithium ions, but is impermeable to other species such as polysulphides, redox mediators and other crossover species. In addition to high Li^+ conductivity, high Li^+ transport number, stability with liquid electrolytes and low interfacial impedance, a key requirement of LICMs is clearly the ability to block crossover species [36,39–41]. Few studies have looked at permeability of LICMs to crossover species in Li-O_2 batteries. Recently, Kim et al. [52] used ex-situ XRD and XPS analysis of the lithium surface after cycling in a Li-O_2 cell to check for reaction with oxygen, water and cathode binder decomposition products. A similar approach was applied to Li-ion cells by MahootcheianAsl et al. [53] who used ex-situ TEM and EDX of the graphite anode surface after cycling, to check for Mn crossover. Other, in-situ but indirect, approaches to measuring electrode ‘crosstalk’ have been applied to Li-ion cells, such as analysis of the voltage drop and capacity fade during storage of graphite-$LiCoO_2$ cells [35].

Permeability of LICMs to polysulphides has been more widely studied. To date, however, this has generally relied on visual inspection or spectroscopic analysis of electrolytes in (or from) a two-compartment, H-type cell [54–57], ex-situ analysis of the membrane (e.g. using SEM/EDX [55,58] or XAS [59] to test for solubility/trapping of polysulphides within it), and/or ex-situ analysis of the lithium anode surface after cycling to test for formation of Li_2S [60–63]. Polysulphide crossover is also typically inferred from cycling performance (upper plateau capacity, capacity retention, Coulombic efficiency, complete charging) [1–8] or self-discharge behaviour of Li-S cells [64]. However, more direct electrochemical techniques have also been applied. Li et al. [65] placed a polysulphide solution in one compartment of an H-type cell, and evaluated the concentration of polysulphides in the other compartment, which was separated by a polymer membrane, using voltammetry and square wave voltammetry at a glassy carbon working electrode. Cui et al. [66] employed a similar approach, in this case measuring rate of diffusion of polysulphides through separators using linear sweep voltammetry in a two-electrode Swagelok cell with stainless steel working electrode. Dominiko et al. [67] developed a method to measure polysulphide concentration in a modified, four-electrode Swagelok cell containing two perpendicular electrodes (nickel and platinum wires) in addition to the lithium and sulphur composite electrodes. Cyclic voltammograms were measured between the perpendicular electrodes at regular intervals during galvanostatic discharge of the Li-S cell and integration of the cathodic peak between 1.5 and 2.25 V was used to determine the concentration of polysulphides. Vizintin et al. [68] later applied this method to evaluate shuttle suppression by a functionalised graphene membrane. Lacey et al. [69] developed a similar approach using a pouch cell with a platinum micro-electrode sensor to detect polysulphides during Li-S battery operation.

All of these approaches bring valuable insights into the mechanism of Li-S batteries and the performance of membranes. However, interpretation is difficult because of the complex electrochemistry of polysulphide species. Whilst several cell designs have been reported for the detection of polysulphide crossover, we are not aware of any article that has tested the cell design with a model and well-behaved electrochemical system.

Here we report a simple, in-situ and direct approach for measuring permeability of LICMs to crossover species, and use ethyl viologen as a model redox system to evaluate its performance. By using a model system, we are able to identify the choice of cell design (working electrode material) and measurement technique that provides the most sensitive, stable and reproducible response.

2. Experimental

Fig. 1A and B illustrate the cell design that has been developed. A glassy carbon working electrode or ‘probe’ (3 mm diameter, type 2, Alfa Aesar) is embedded in a 1-inch diameter glass disc attached to a glass tube. A thin copper rod in contact with the back face of the glassy carbon serves as the current collector. For some experiments, other working electrodes were used (Fig. 1C): copper (1/2 inch diameter (nominal; 12.65 mm measured) HDHC rod, 99.9%, RS), stainless steel (1/2 inch diameter 316 stainless steel rod, RS) and aluminium (1/2 inch diameter 2011i aluminium rod, RS).

Prior to use, glassy carbon electrodes were polished with 25, 3.0 and 0.3 μm alumina powder in deionised water (Purite, 18.2 MΩ cm). Lithium ion conducting glass ceramic (LICGC™) plates (1 inch diameter, 150 μm thickness, Ohara Inc.) were sonicated in isopropyl alcohol (Fisher Scientific, 99.5%). Both were dried under vacuum at 80 °C for a minimum of 30 min. Copper, stainless steel and aluminium electrodes were cleaned either mechanically (sanded and polished in ethanol) or chemically (dipped in 70% nitric acid for 5 s, rinsed with deionised water then ethanol), and dried under vacuum at 80 °C for 10 min only, to minimise reformation of a surface oxide layer.

$Li_{0.5}FePO_4$ electrodes were used as both counter and reference electrodes and were prepared by mixing $LiFePO_4$ (battery grade, Tatung), $FePO_4$ (prepared in-house by delithiating $LiFePO_4$ [70]), carbon black (acetylene, 100% compressed, Chevron Philips) and PTFE (6CN, DuPont) in the ratio 4:4:1:4 (wt%) in a pestle and mortar. The composite material was roll-pressed to a thickness of 100 μm and punched to the required diameter (10 mm for cells with glassy carbon working electrode, 12 mm for cells with other working electrodes).

$Li_{0.5}FePO_4$ electrodes and glass fibre separators (Whatman, 300 μm thickness, punched to required 10 or 12 mm diameter) were dried under vacuum at 120 °C for 24 h. Celgard (2320, punched to required 25 mm diameter) was dried under vacuum, unheated, for 24 h.

For the electrolytes, ethyl viologen triflate ($EtV(OTf)_2$) was prepared in-house according to the literature [71] from ethyl viologen di-iodide ($EtVI_2$, 99%, Sigma-Aldrich) and silver triflate (AgOTf, ≥99%, Sigma-Aldrich). 1-butyl-1-methylpyrrolidinum bis(trifluoromethylsulfonyl)imide ($Pyr_{14}TFSI$) (99%, IoLiTec Ionic Liquids Technologies GmbH) and lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI) (99.95%, Sigma-Aldrich) were dried and deoxygenated under vacuum at 120 °C for 24 h. Electrolytes (0–4 mM $EtV(OTf)_2$ + 100 mM LiTFSI in $Pyr_{14}TFSI$) were prepared inside an argon filled glovebox (<1 ppm water content, < 10 ppm oxygen content, M-Braun). Cells were assembled inside the same glovebox. When assembling cells, 30 μl of electrolyte was used for each 10 mm separator (50 μl for 12 mm separators).

Electrochemical measurements were carried out using a Biologic VMP2 variable multichannel potentiostat/galvanostat. Square wave voltammetry scans were carried out with the following parameters: $\Delta E_s = 10$ mV, $\Delta E_p = 25$ mV, $t_p = 50$ ms. All measurements were carried out at a controlled temperature of 25 °C.