**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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**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-O2 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-O2 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-O2 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 Li2O2 and/or to reduce high overpotentials for oxygen reduction/evolution [1], [12-32].

The issue of crossover is not confined to Li-S and Li-O2 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-O2 batteries. Recently, Kim et al [52] used ex-situ XRD and XPS analysis of the lithium surface after cycling in a Li-O2 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-LiCoO2 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 Li2S [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-electrodes 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**

Figure 1A,B illustrates 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 (Figure 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 (LICGCTM) 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 ⁰C for a minimum of 30 minutes. Copper, stainless steel and aluminium electrodes were cleaned either mechanically (sanded and polished in ethanol) or chemically (dipped in 70% nitric acid for 5 seconds, rinsed with deionised water then ethanol), and dried under vacuum at 80 ⁰C for 10 minutes only, to minimise reformation of a surface oxide layer.

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**Figure 1. Sketch of Swagelok cell with glassy carbon electrode used for the characterization of membrane permeability (A) or electrochemical properties of the redox species (B), and sketch of Swagelok cell used with other working electrodes (C).**

Li0.5FePO4 electrodes were used as both counter and reference electrodes and were prepared by mixing LiFePO4 (battery grade, Tatung), FePO4 (prepared in-house by delithiating LiFePO4 [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).

Li0.5FePO4 electrodes and glass fibre separators (Whatman, 300 μm thickness, punched to required 10 or 12 mm diameter) were dried under vacuum at 120 ⁰C for 24 hours. Celgard (2320, punched to required 25 mm diameter) was dried under vacuum, unheated, for 24 hours.

For the electrolytes, ethyl viologen triflate (EtV(OTf)2) was prepared in-house according to the literature [71] from ethyl viologen di-iodide (EtVI2, 99%, Sigma-Aldrich) and silver triflate (AgOTf, ≥99%, Sigma-Aldrich). 1-butyl-1-methylpyrrolidinum bis(trifluoromethylsulfonyl)imide (Pyr14TFSI) (99%, IoLiTec Ionic Liquids Technologies GmbH) and lithium bis(trifluoromethane)-sulfonamide salt (LiTFSI) (99.95%, Sigma-Aldrich) were dried and deoxygenated under vacuum at 120 ⁰C for 24 hours. Electrolytes (0–4 mM EtV(OTf)2 + 100 mM LiTFSI in Pyr14TFSI) 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 Bio-logic VMP2 variable multichannel potentiostat/galvanostat. Square wave voltammetry scans were carried out with the following parameters: Δ*E*s = 10 mV, Δ*E*р = 25 mV, tp = 50 ms. All measurements were carried out at a controlled temperature of 25 ⁰C.

**3. Results**

***3.1. Using square wave voltammetry to characterise crossover redox species***

In conventional cyclic voltammetry, both Faradaic and non-Faradaic (double layer charging) processes contribute to the measured current. If the concentration of redox species is low, the non-Faradaic currents can dominate. To overcome this, pulsed voltammetry techniques can be employed, which essentially strip out the non-Faradaic contribution from the signal. This is done by applying a series of potential ‘pulses’ and sampling the current after such time that the double-layer current has decayed but the Faradaic current is still high. The exact form of the applied potential profile depends on the particular pulse technique. Square wave voltammetry (SWV) combines advantages (sensitivity, background suppression, diagnostic value) of several pulse voltammetry methods [72].

The application of square wave voltammetry to a model redox system (ethyl viologen, EtV2+) is illustrated in Figure 2. The applied voltage profile is shown in Figure 2A. It starts well positive of the formal potential, *E*0’, of the EtV2+/EtV+ couple, and consists of a series of forward and reverse pulses which are superimposed on an underlying ‘staircase’. The profile can be described by a starting potential *E*i, a staircase step height Δ*E*р, a pulse height, Δ*E*р, and a pulse width, *t*p, as indicated in Figure 2A. Figure 2B shows the evolution of the current response vs. time. Current is sampled at the end of the forward and reverse pulses, at the points highlighted in green and red, respectively. Figure 2C shows just the sampled forward (*i*f) and reverse (*i*r) currents vs. time, together with a ‘difference current’, Δ*i*, which is the difference between the sampled forward and reverse currents: Δ*i* = *i*f – *i*r . The time axis in Figure 2C is converted to a potential axis in Figure 2D.

At the start of the scan, the currents are small (for both the forward and reverse pulses) as the potential remains well positive of *E*0’, and thus little electrochemistry is induced by the potential pulses (Figure 2B). The difference in the current sampled at the forward and reverse pulses is also very small (Figure 2C,D). In the middle of the scan, close to *E*0’, the current depends strongly on potential: the forward pulse significantly increases the rate of reduction of EtV2+, while the reverse pulse reverses the direction of current flow as EtV+ is oxidised back to EtV2+ (Figure 2B). Indeed, the difference in current sampled at the end of the forward and reverse pulses goes through a maximum at potentials close to *E*0’ (Figure 2D). Finally, at the end of the scan, the applied staircase potential is well negative of *E*0’ and the rate of reaction is diffusion-controlled (Figure 2B); as a result, the current sampled in the forward and reverse pulses are very similar and the difference in current is small (Figure 2C,D).

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**Figure 2. A) Voltage profile applied in square wave voltammetry with *E*i = -0.7 V vs Li0.5FePO4/Li+, Δ*E*s = 10 mV, Δ*E*р = 25 mV, *t*p = 50 ms (only the start of the profile is shown for clarity). B) Resulting current profile measured in a solution containing ethyl viologen; the green and red dots highlight the times at which the current is sampled in the forward and reverse pulses, respectively. C,D) Values of the current sampled in the forward (–) and reverse (–) pulses, and difference in forward and reverse currents (–), plotted vs. time (C) or potential (D). Measurements were recorded in cell with glassy carbon working electrode, Li0.5FePO4 counter/reference electrode and 2 mM EtV(OTf)2 + 100 mM LiTFSi in Pyr14TSFI electrolyte. See cell sketch in Figure 1B.**

In conclusion, the square wave voltammogram, which is a plot of the difference in current sampled at the forward and reverse pulses, Δ*i* = *i*f – *i*r, vs. potential, is shown to exhibit a maximum at potentials close to *E*0’, as shown in Figure 2D. For a simple, reversible electrochemical reaction, and if only oxidized species are initially present in solution, the potential at which the peak difference current occurs is given by:

 $E\_{1/2} = E^{0'} + (RT/nF)ln(D\_{R}/D\_{O})^{1/2}$ (Eq. 1)

where $D\_{R}$ and $D\_{O}$ are the diffusion coefficients of the reduced, and oxidized species, respectively, R is the gas constant, T is the temperature in Kelvin, n is the number of electrons and F is the Faraday constant. The peak difference current is given by:

$$∆i\_{p} =\frac{nFD\_{O}^{1/2}c\_{O}^{\*}}{π^{1/2}t\_{p}^{1/2}}∆ψ\_{p}$$

 (Eq. 2)

where $c\_{O}^{\*} $is the initial concentration of the oxidized species and Δ*ψ*p is a dimensionless parameter that is a function of Δ*E*s and Δ*E*p. Computed values for Δ*ψ*p are availablein the literature [73, 74]; for Δ*E*s = 10 mV and Δ*E*р = 25 mV, Δ*ψ*p = 0.569.

***3.2. Testing of alternative probe materials and techniques***

To investigate the performance of our glassy carbon probe with square wave voltammetry, initial experiments were conducted using a cell without a membrane, i.e. with a single glass fibre separator soaked with electrolyte containing ethyl viologen (Figure 1B). This can be done because the standard potential of the Li0.5FePO4 counter/reference electrode (ca. 3.45 V vs. Li/Li+) is more positive than that of ethyl viologen (ca. 2.43 V vs. Li/Li+). Therefore EtV2+ is stable in contact with the Li0.5FePO4. The reaction products of EtV2+ (i.e. EtV+ or EtV) would be oxidised by Li0.5FePO4 but the timescale of the square wave voltammograms is much shorter than the timescale for these products to diffuse across the cell. In addition, the amount of EtV+ or EtV produced is far too small to change the bulk concentration of the electrolyte within the separator.

Figure 3 shows the reproducibility of square wave voltammograms recorded in two separate cells with a glassy carbon working electrode, a Li0.5FePO4 counter/reference electrode and 2 mM EtV(OTf)2 in the electrolyte. The initial sweep was in the cathodic direction. The EtV2+/EtV+ and EtV+/EtV redox couples are clearly visible at ca. 2.02 V and 2.43 V vs. Li/Li+. The measurements are highly reproducible and stable with cycling. Differences between cells are not visible in this scale, and an expanded view is provided in Figure S1.



**Figure 3. Comparison of square wave voltammograms recorded at a glassy carbon electrode in two separate cells, (―) and (―), containing 2mM EtV(OTf)2 in the electrolyte. All experimental conditions as in Figure 2, except *E*i = -0.3 V vs Li0.5FePO4/Li+.**

Figure 4A compares square wave voltammograms recorded at the glassy carbon electrode and at the best-performing copper electrode, which had been treated mechanically. It can be seen that, relative to the glassy carbon electrode, the copper electrode is less sensitive (lower ratio of peak current to residual double layer charging current) and less reliable (shows distortions from other redox processes). These differences are even more apparent when comparing cyclic voltammograms (Figure 4B), with the copper electrode showing a small reduction peak at ca. 1.78 V vs. Li/Li+ together with an additional broad oxidation peak/shoulder at ca. 2.65 **–** 3.05 V vs. Li/Li+. Based on cyclic voltammetry at a copper electrode in a cell without EtV(OTf)2 (Figure S2), these peaks are attributed to lithium insertion into a residual copper oxide surface layer [75]. Measurements with the copper working electrode were also less stable and less reproducible than those with the glassy carbon electrode (Figure S3). The performance of chemically- treated copper electrodes showed no improvement over those treated mechanically, with the same additional peaks, large background current, and poor stability and reproducibility (Figure S4). The performance of (mechanically treated) electrodes made from stainless steel or aluminium were also much poorer than that of glassy carbon (Figure S5). Scans recorded at stainless steel electrodes required several conditioning cycles to achieve (temporarily) stable peak heights, which nevertheless deteriorated over time. Aluminium showed blocking behaviour due to passivation especially at more positive potentials, resulting in poor sensitivity (small peak to background current ratio). It also showed large distortion at low potentials, possibly due to surface redox activity, and poor stability.

 

**Figure 4. Square wave voltammograms (A) and cyclic voltammograms (B) recorded at a glassy carbon electrode (―) and mechanically-treated copper electrode (―) in cells containing 2mM EtV(OTf)2 in the electrolyte. The cells used are sketched in Figure 1B (glassy carbon electrode) and Figure 1C (copper electrode). All experimental conditions as in Figure 3. CV scan rate 20 mV s-1.**

Figure 5 demonstrates the advantage of square wave voltammetry over cyclic voltammetry at low concentrations (10 μM) of redox species. Although the peaks corresponding to the ethyl viologen redox couples are weak, they are still clearly distinguishable in the square wave voltammogram, in contrast to the cyclic voltammogram. The number of moles of EtV(OTf)2 present in this cell is just 3 x 10-10, and could be decreased further by using thinner separators.



 **Figure 5. Square wave voltammogram (A) and cyclic voltammogram (B) recorded at a glassy carbon electrode in a cell containing 10 μM EtV(OTf)2 in the electrolyte. All other experimental conditions as in Figure 4.**

***3.3. Testing for electrolyte leakage***

In order to verify that the cell is well-sealed with gaskets, an LICGC™ plate supplied by Ohara Inc. was added to the cell, with EtV(OTf)2 placed on the counter electrode side of this membrane only. LICGC™ is a single (lithium) ion conductor and therefore the only way for ethyl viologen species to pass from the counter to working electrode compartments would be via leakage of electrolyte around the edges of the membrane. However, no redox peaks relating to ethyl viologen appeared in square-wave voltammograms recorded over a two week period (Figure 6), confirming no such leakage.



**Figure 6. Square wave voltammograms recorded at a glassy carbon electrode at the start (solid line) and end (dashed line) of a two week period, in a cell containing 2mM EtV(OTf)2 in the counter/reference electrode compartment, which is separated from the working electrode compartment by a LICGCTM membrane. See cell sketch in Fig. 1A. Other experimental conditions as in Figure 3.**

***3.4. Cell calibration***

According to equation 2, the size of the peak difference current in square wave voltammetry can be used to determine the concentration of redox species if the diffusion coefficient in the electrolyte is known. In order to estimate the effective diffusion coefficient of EtV2+ in our system, the glassy carbon electrode was used to record square wave voltammograms for several known EtV2+ concentrations. Figure 7 shows the resulting plot of Δ*i*p versus concentration, which yields a value for the diffusion coefficient of 7.5 x 10-8 cm2 s-1 for EtV2+ in the electrolyte when soaked into a glass fibre separator.



**Figure 7. Peak difference current for EtV2+/EtV+ reduction from square-wave voltammograms recorded at a glassy carbon electrode in cells containing 0.1 – 2mM EtV(OTf)2 in the electrolyte. Other experimental conditions as in Figure 3.**

***3.5. Measuring permeability of a membrane to crossover species***

As a proof of concept of the method, a cell was constructed with a permeable membrane (Celgard). As before, EtV(OTf)2 was placed in the counter/reference electrode compartment only. In this case we would expect peaks corresponding to ethyl viologen redox processes to appear over time as EtV2+ passes through the Celgard. Figure 8A demonstrates this phenomenon. No redox peaks are visible initially but gradually appear and grow as the concentration of EtV2+ in the working electrode compartment increases. As described above, equation 2 can be used to calculate this concentration from the size of the peak difference current, and, as expected, it tends to a value of *ca.* 2 mM (Figure 8B), indicating that the initial 0 mM and 4 mM concentrations in the working and counter electrode compartments, respectively, have equilibrated.



**Figure 8. A) Square wave voltammograms recorded at a glassy carbon electrode at 15 minute intervals in a cell containing 4mM EtV(OTf)2 in the counter/reference electrode compartment, which is separated from the working electrode compartment, which initially contains no EtV(OTf)2, by a Celgard membrane. See cell sketch in Figure 1A. Other experimental conditions as in Figure 2. B) EtV2+ concentration in the working electrode compartment over time, derived from peak difference currents in Figure 8A.**

**4. Conclusions**

We have demonstrated a convenient, in-situ, direct and quantitative method for measuring permeability of LICMs to crossover species. While several cell designs have been reported for the detection of polysulphide crossover in Li-S systems, we are not aware of any other article that has tested the cell design with a model and well-behaved electrochemical system. We have found that, by testing our method with ethyl viologen, we were able to identify the electrode material that gave a more sensitive (lower limit of detection), reproducible and reliable (free from distortions) response. We were also able to prove that using a differential technique like square wave voltammetry produced a major increase in the sensitivity of the measurements, compared to other techniques such as cyclic voltammetry. This is because square wave voltammetry is able to separate the redox reaction of the crossover species from other processes such as double-layer charging.

Employing a glassy carbon electrode to record square wave voltammograms provides a sensitive, stable and reproducible means to detect crossover species, with glassy carbon performing better than other working electrode materials and square wave voltammetry performing better than other types of voltammetry. The new cell design allows testing of membrane permeability using small electrolyte volumes (35 μl) and can detect molar quantities less than 10-9 moles and concentrations of less than 10 µM. The facile, in-situ measurement procedure makes it possible to record any passage of redox species through the membrane in real time using a single cell. The quantitative nature of the measurements allows the rate of passage to be determined.

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**References**

[1] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, Li-O2 and Li-S batteries with high energy storage, Nat. Mater., 11 (2012) 19-29.

[2] X. Ji, L.F. Nazar, Advances in Li-S batteries, J. Mater. Chem., 20 (2010) 9821-9826.

[3] Y.V. Mikhaylik, J.R. Akridge, Polysulfide shuttle study in the Li/S battery system, J. Electrochem. Soc., 151 (2004) A1969-A1976.

[4] M. Wild, L. O'Neill, T. Zhang, R. Purkayastha, G. Minton, M. Marinescu, G.J. Offer, Lithium sulfur batteries, a mechanistic review, Energy Environ. Sci., 8 (2015) 3477-3494.

[5] S. Urbonaite, T. Poux, P. Novák, Progress towards commercially viable Li–S battery cells, Adv. Energy Mater., 5 (2015).

[6] R.P. Martin, W.H. Doub, J.L. Roberts, D.T. Sawyer, Electrochemical reduction of sulfur in aprotic solvents, Inorg. Chem., 12 (1973) 1921-1925.

[7] R.D. Rauh, F.S. Shuker, J.M. Marston, S.B. Brummer, Formation of lithium polysulfides in aprotic media, J. Inorg. Nucl. Chem., 39 (1977) 1761-1766.

[8] E. Peled, Y. Sternberg, A. Gorenshtein, Y. Lavi, Lithium‐sulfur battery: Evaluation of dioxolane‐based electrolytes, J. Electrochem. Soc., 136 (1989) 1621-1625.

[9] M. Roberts, R. Younesi, W. Richardson, J. Liu, T. Gustafsson, J. Zhu, K. Edström, Increased cycling efficiency of lithium anodes in dimethyl sulfoxide electrolytes for use in Li-O2 batteries, ECS Electrochem. Lett., 3 (2014) A62-A65.

[10] R.S. Assary, J. Lu, P. Du, X. Luo , X. Zhang, Y. Ren, L.A. Curtiss, K. Amine, The effect of oxygen crossover on the anode of a Li-O2 battery using an ether-based solvent: Insights from experimental and computational studies, ChemSusChem, 6 (2013) 51-55.

[11] X. Yao, Q. Dong, Q. Cheng, D. Wang, Why do lithium–oxygen batteries fail: Parasitic chemical reactions and their synergistic effect, Angew. Chem. Int. Ed., 55 (2016) 11344-11353.

[12] Y. Chen, S.A. Freunberger, Z. Peng, O. Fontaine, P.G. Bruce, Charging a Li-O2 battery using a redox mediator, Nat. Chem., 5 (2013) 489-494.

[13] M.J. Lacey, J.T. Frith, J.R. Owen, A redox shuttle to facilitate oxygen reduction in the lithium air battery, Electrochem. Commun., 26 (2013) 74-76.

[14] B.J. Bergner, A. Schürmann, K. Peppler, A. Garsuch, J. Janek, Tempo: A mobile catalyst for rechargeable Li-O2 batteries, J. Am. Chem. Soc., 136 (2014) 15054-15064.

[15] D. Sun, Y. Shen, W. Zhang, L. Yu, Z. Yi, W. Yin, D. Wang, Y. Huang, J. Wang, D. Wang, J.B. Goodenough, A solution-phase bifunctional catalyst for lithium–oxygen batteries, J. Am. Chem. Soc., 136 (2014) 8941-8946.

[16] Y.G. Zhu, C. Jia, J. Yang, F. Pan, Q. Huang, Q. Wang, Dual redox catalysts for oxygen reduction and evolution reactions: Towards a redox flow Li-O2 battery, Chem. Commun., 51 (2015) 9451-9454.

[17] M. Yu, X. Ren, L. Ma, Y. Wu, Integrating a redox-coupled dye-sensitized photoelectrode into a lithium–oxygen battery for photoassisted charging, Nat. Commun., 5 (2014).

[18] D.S. Kim, Y.J. Park, Effect of multi-catalysts on rechargeable Li–air batteries, J. Alloys Compd., 591 (2014) 164-169.

[19] T.H. Yoon, Y.J. Park, New strategy toward enhanced air electrode for Li-air batteries: Apply a polydopamine coating and dissolved catalyst, RSC Adv., 4 (2014) 17434-17442.

[20] H.-D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K.-Y. Park, J. Hong, H. Kim, T. Kim, Y.H. Kim, X. Lepró, R. Ovalle-Robles, R.H. Baughman, K. Kang, Superior rechargeability and efficiency of lithium–oxygen batteries: Hierarchical air electrode architecture combined with a soluble catalyst, Angew. Chem., 126 (2014) 4007-4012.

[21] W.-J. Kwak, D. Hirshberg, D. Sharon, H.-J. Shin, M. Afri, J.-B. Park, A. Garsuch, F.F. Chesneau, A.A. Frimer, D. Aurbach, Y.-K. Sun, Understanding the behavior of Li-oxygen cells containing LiI, J. Mater. Chem. A, 3 (2015) 8855-8864.

[22] T. Liu, M. Leskes, W. Yu, A.J. Moore, L. Zhou, P.M. Bayley, G. Kim, C.P. Grey, Cycling Li-O2 batteries via LiOH formation and decomposition, Science, 350 (2015) 530-533.

[23] X. Zeng, L. Leng, F. Liu, G. Wang, Y. Dong, L. Du, L. Liu, S. Liao, Enhanced Li-O2 battery performance, using graphene-like nori-derived carbon as the cathode and adding LiI in the electrolyte as a promoter, Electrochim. Acta, 200 (2016) 231-238.

[24] T. Zhang, K. Liao, P. He, H. Zhou, A self-defense redox mediator for efficient lithium-O2 batteries, Energy Environ. Sci., 9 (2016) 1024-1030.

[25] I. Landa-Medrano, M. Olivares-Marín, R. Pinedo, I. Ruiz de Larramendi, T. Rojo, D. Tonti, Operando UV-visible spectroscopy evidence of the reactions of iodide as redox mediator in Li-O2 batteries, Electrochem. Commun., 59 (2015) 24-27.

[26] D. Kundu, R. Black, B. Adams, L.F. Nazar, A highly active low voltage redox mediator for enhanced rechargeability of lithium–oxygen batteries, ACS Cent. Sci., 1 (2015) 510-515.

[27] Z. Liang, Y.-C. Lu, Critical role of redox mediator in suppressing charging instabilities of lithium–oxygen batteries, J. Am. Chem. Soc., 138 (2016) 7574-7583.

[28] A.Y. Tesio, D. Blasi, M. Olivares-Marin, I. Ratera, D. Tonti, J. Veciana, Organic radicals for the enhancement of oxygen reduction reaction in Li-O2 batteries, Chem. Commun., 51 (2015) 17623-17626.

[29] Y.G. Zhu, Q. Liu, Y. Rong, H. Chen, J. Yang, C. Jia, L.-J. Yu, A. Karton, Y. Ren, X. Xu, S. Adams, Q. Wang, Proton enhanced dynamic battery chemistry for aprotic lithium–oxygen batteries, Nat. Commun., 8 (2017).

[30] X. Gao, Y. Chen, L. Johnson, P.G. Bruce, Promoting solution phase discharge in Li-O2 batteries containing weakly solvating electrolyte solutions, Nat. Mater., 15 (2016) 882-888.

[31] W.-J. Kwak, D. Hirshberg, D. Sharon, M. Afri, A.A. Frimer, H.-G. Jung, D. Aurbach, Y.-K. Sun, Li-O2 cells with LiBr as an electrolyte and a redox mediator, Energy Environ. Sci., 9 (2016) 2334-2345.

[32] C.M. Burke, R. Black, I.R. Kochetkov, V. Giordani, D. Addison, L.F. Nazar, B.D. McCloskey, Implications of 4 e– oxygen reduction via iodide redox mediation in Li-O2 batteries, ACS Energy Lett., 1 (2016) 747-756.

[33] T. Joshi, K. Eom, G. Yushin, T.F. Fuller, Effects of dissolved transition metals on the electrochemical performance and SEI growth in lithium-ion batteries, J. Electrochem. Soc., 161 (2014) A1915-A1921.

[34] C. Zhan, J. Lu, A. Jeremy Kropf, T. Wu, A.N. Jansen, Y.-K. Sun, X. Qiu, K. Amine, Mn(II) deposition on anodes and its effects on capacity fade in spinel lithium manganate–carbon systems, Nat. Commun., 4 (2013) 2437.

[35] N.N. Sinha, A.J. Smith, J.C. Burns, G. Jain, K.W. Eberman, E. Scott, J.P. Gardner, J.R. Dahn, The use of elevated temperature storage experiments to learn about parasitic reactions in wound LiCoO2/graphite cells, J. Electrochem. Soc., 158 (2011) A1194-A1201.

[36] N. Deng, W. Kang, Y. Liu, J. Ju, D. Wu, L. Li, B.S. Hassan, B. Cheng, A review on separators for lithium–sulfur battery: Progress and prospects, J. Power Sources, 331 (2016) 132-155.

[37] D. Moy, S.R. Narayanan, Mixed conduction membranes suppress the polysulfide shuttle in lithium-sulfur batteries, J. Electrochem. Soc., 164 (2017) A560-A566.

[38] K. Xie, K. Yuan, K. Zhang, C. Shen, W. Lv, X. Liu, J.-G. Wang, B. Wei, Dual functionalities of carbon nanotube films for dendrite-free and high energy–high power lithium–sulfur batteries, ACS Appl. Mater. Interfaces, 9 (2017) 4605-4613.

[39] J. Christensen, P. Albertus, R.S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojic, A critical review of Li/air batteries, J. Electrochem. Soc., 159 (2011) R1-R30.

[40] Y. Sun, Lithium ion conducting membranes for lithium-air batteries, Nano Energy, 2 (2013) 801-816.

[41] M.R. Busche, T. Drossel, T. Leichtweiss, D.A. Weber, M. Falk, M. Schneider, M.-L. Reich, H. Sommer, P. Adelhelm, J. Janek, Dynamic formation of a solid-liquid electrolyte interphase and its consequences for hybrid-battery concepts, Nat. Chem., 8 (2016) 426-434.

[42] B.J. Bergner, M.R. Busche, R. Pinedo, B.B. Berkes, D. Schröder, J. Janek, How to improve capacity and cycling stability for next generation Li-O2 batteries: Approach with a solid electrolyte and elevated redox mediator concentrations, ACS Appl. Mater. Interfaces, 8 (2016) 7756-7765.

[43] D.J. Lee, H. Lee, Y.-J. Kim, J.-K. Park, H.-T. Kim, Sustainable redox mediation for lithium–oxygen batteries by a composite protective layer on the lithium-metal anode, Adv. Mater., 28 (2016) 857-863.

[44] T.T. Truong, Y. Qin, Y. Ren, Z. Chen, M.K. Chan, J.P. Greeley, K. Amine, Y. Sun, Single-crystal silicon membranes with high lithium conductivity and application in lithium-air batteries, Adv. Mater., 23 (2011) 4947-4952.

[45] H.T.T. Le, R.S. Kalubarme, D.T. Ngo, H.S. Jadhav, C.-J. Park, Bi-layer lithium phosphorous oxynitride/aluminium substituted lithium lanthanum titanate as a promising solid electrolyte for long-life rechargeable lithium-oxygen batteries, J. Mater. Chem. A, 3 (2015) 22421-22431.

[46] H.T.T. Le, D.T. Ngo, V.-C. Ho, G. Cao, C.-N. Park, C.-J. Park, Insights into degradation of metallic lithium electrodes protected by a bilayer solid electrolyte based on aluminium substituted lithium lanthanum titanate in lithium-air batteries, J. Mater. Chem. A, 4 (2016) 11124-11138.

[47] J. Kumar, P. Kichambare, A.K. Rai, R. Bhattacharya, S. Rodrigues, G. Subramanyam, A high performance ceramic-polymer separator for lithium batteries, J. Power Sources, 301 (2016) 194-198.

[48] H.S. Jadhav, R.S. Kalubarme, A.H. Jadhav, J.G. Seo, Highly stable bilayer of LiPON and B2O3 added Li1.5Al0.5Ge1.5(PO4) solid electrolytes for non-aqueous rechargeable Li-O2 batteries, Electrochim. Acta, 199 (2016) 126-132.

[49] J. Yi, S. Guo, P. He, H. Zhou, Status and prospects of polymer electrolytes for solid-state Li-O2 (air) batteries, Energy Environ. Sci., 10 (2017) 860-884.

[50] L. Leng, X. Zeng, P. Chen, T. Shu, H. Song, Z. Fu, H. Wang, S. Liao, A novel stability-enhanced lithium-oxygen battery with cellulose-based composite polymer gel as the electrolyte, Electrochim. Acta, 176 (2015) 1108-1115.

[51] G.A. Elia, J. Hassoun, A gel polymer membrane for lithium-ion oxygen battery, Solid State Ionics, 287 (2016) 22-27.

[52] B.G. Kim, J.-S. Kim, J. Min, Y.-H. Lee, J.H. Choi, M.C. Jang, S.A. Freunberger, J.W. Choi, A moisture- and oxygen-impermeable separator for aprotic Li-O2 batteries, Adv. Funct. Mater., 26 (2016) 1747-1756.

[53] N. MahootcheianAsl, J.-H. Kim, N.P.W. Pieczonka, Z. Liu, Y. Kim, Multilayer electrolyte cell: A new tool for identifying electrochemical performances of high voltage cathode materials, Electrochem. Commun., 32 (2013) 1-4.

[54] J. Conder, A. Forner-Cuenca, E.M. Gubler, L. Gubler, P. Novák, S. Trabesinger, Performance-enhancing asymmetric separator for lithium–sulfur batteries, ACS Appl. Mater. Interfaces, 8 (2016) 18822-18831.

[55] X. Yu, Z. Bi, F. Zhao, A. Manthiram, Hybrid lithium–sulfur batteries with a solid electrolyte membrane and lithium polysulfide catholyte, ACS Appl. Mater. Interfaces, 7 (2015) 16625-16631.

[56] J.-Q. Huang, Q. Zhang, H.-J. Peng, X.-Y. Liu, W.-Z. Qian, F. Wei, Ionic shield for polysulfides towards highly-stable lithium-sulfur batteries, Energy Environ. Sci., 7 (2014) 347-353.

[57] X.-l. Wu, J. Zong, H. Xu, W. Wang, X.-j. Liu, Effects of LAGP electrolyte on suppressing polysulfide shuttling in Li-S cells, RSC Adv., 6 (2016) 57346-57356.

[58] W. Cai, G. Li, F. He, L. Jin, B. Liu, Z. Li, A novel laminated separator with multi functions for high-rate dischargeable lithium–sulfur batteries, J. Power Sources, 283 (2015) 524-529.

[59] I. Villaluenga, K.H. Wujcik, W. Tong, D. Devaux, D.H.C. Wong, J.M. DeSimone, N.P. Balsara, Compliant glass–polymer hybrid single ion-conducting electrolytes for lithium batteries, Proc. Natl. Acad. Sci. U.S.A., 113 (2016) 52-57.

[60] X. Yu, J. Joseph, A. Manthiram, Polymer lithium-sulfur batteries with a Nafion membrane and an advanced sulfur electrode, J. Mater. Chem. A, 3 (2015) 15683-15691.

[61] F. Zeng, Z. Jin, K. Yuan, S. Liu, X. Cheng, A. Wang, W. Wang, Y.-s. Yang, High performance lithium-sulfur batteries with a permselective sulfonated acetylene black modified separator, J. Mater. Chem. A, 4 (2016) 12319-12327.

[62] M. Liu, D. Zhou, Y.-B. He, Y. Fu, X. Qin, C. Miao, H. Du, B. Li, Q.-H. Yang, Z. Lin, T.S. Zhao, F. Kang, Novel gel polymer electrolyte for high-performance lithium–sulfur batteries, Nano Energy, 22 (2016) 278-289.

[63] J. Zhu, Y. Ge, D. Kim, Y. Lu, C. Chen, M. Jiang, X. Zhang, A novel separator coated by carbon for achieving exceptional high performance lithium-sulfur batteries, Nano Energy, 20 (2016) 176-184.

[64] S.M. Al-Mahmoud, J.W. Dibden, J.R. Owen, G. Denuault, N. Garcia-Araez, A simple, experiment-based model of the initial self-discharge of lithium-sulphur batteries, J. Power Sources, 306 (2016) 323-328.

[65] C. Li, A.L. Ward, S.E. Doris, T.A. Pascal, D. Prendergast, B.A. Helms, Polysulfide-blocking microporous polymer membrane tailored for hybrid Li-sulfur flow batteries, Nano Lett., 15 (2015) 5724-5729.

[66] Y. Cui, Y. Fu, Polysulfide transport through separators measured by a linear voltage sweep method, J. Power Sources, 286 (2015) 557-560.

[67] R. Dominko, R. Demir-Cakan, M. Morcrette, J.-M. Tarascon, Analytical detection of soluble polysulphides in a modified Swagelok cell, Electrochem. Commun., 13 (2011) 117-120.

[68] A. Vizintin, M.U.M. Patel, B. Genorio, R. Dominko, Effective separation of lithium anode and sulfur cathode in lithium–sulfur batteries, ChemElectroChem, 1 (2014) 1040-1045.

[69] M.J. Lacey, K. Edström, D. Brandell, Analysis of soluble intermediates in the lithium–sulfur battery by a simple in situ electrochemical probe, Electrochem. Commun., 46 (2014) 91-93.

[70] N. Intaranont, N. Garcia-Araez, A.L. Hector, J.A. Milton, J.R. Owen, Selective lithium extraction from brines by chemical reaction with battery materials, J. Mater. Chem. A, 2 (2014) 6374-6377.

[71] L. Yang, J.T. Frith, N. Garcia-Araez, J.R. Owen, A new method to prevent degradation of lithium-oxygen batteries: Reduction of superoxide by viologen, Chem. Commun., 51 (2015) 1705-1708.

[72] A. Bard, L. Faulkner, Electrochemical methods: Fundamentals and applications, John Wiley & Sons, Inc, New York, NY, USA, 2001.

[73] J.G. Osteryoung, R.A. Osteryoung, Square wave voltammetry, Anal. Chem., 57 (1985) 101-110.

[74] J.G. Osteryoung, J.J. O'Dea, in: A.J. Bard (Ed.) Electroanalytical chemistry: A series of advances: Volume 14, Marcel Dekker Inc., New York, NY, USA, 1986, pp. 209–325.

[75] F.-S. Ke, L. Huang, G.-Z. Wei, L.-J. Xue, J.-T. Li, B. Zhang, S.-R. Chen, X.-Y. Fan, S.-G. Sun, One-step fabrication of CuO nanoribbons array electrode and its excellent lithium storage performance, Electrochim. Acta, 54 (2009) 5825-5829.