Mixed Conduction Membranes Suppress the Polysulfide Shuttle in Lithium-Sulfur Batteries

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The shuttling of polysulfide ions between the two electrodes of a lithium-sulfur battery is a major technical issue that limits the electrical performance and cycle life of this battery. This "polysulfide shuttle" causes self-discharge, low charging efficiencies, and irreversible capacity losses. Suppressing the polysulfide shuttle will bring us closer to realizing a rechargeable battery that has two to three times the energy density of today’s lithium-ion batteries. We demonstrate a novel approach to the problem of the polysulfide shuttle by using a “mixed conduction membrane” (MCM). The MCM is a thin non-porous lithium-ion conducting barrier that simply restricts the soluble polysulfides to the positive electrode. Lithium-ion conduction occurs through the MCM by electrochemical intercalation or insertion reactions and concomitant solid-state diffusion, exactly as in the cathode of a lithium-ion battery. Because of the rapidity of lithium ion transport in the MCM, the internal resistance of the battery is not higher than that of a conventional lithium-sulfur battery. The MCM is as effective as the lithium nitrate additive in suppressing the polysulfide shuttle reactions. However, unlike lithium nitrate, the MCM is not used up during cycling and thus provides extended durability and cycle life. We establish the criteria for the selection of materials for MCMs and demonstrate the effectiveness of this novel MCM layer by proving the suppression of shuttling of polysulfides, demonstration of improved capacity retention during repeated cycling, and by the preservation of rate capability and impedance of the lithium-sulfur battery.

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Despite many advances in the area of lithium-ion batteries, the demand for more compact, lightweight, and long-life batteries for portable and automotive applications has continued to steadily increase. Thus, the search for battery solutions with increasingly higher specific energy remains a major quest. The rechargeable lithium-sulfur battery is particularly attractive for high-density electrical energy storage because of its high theoretical specific energy of 2600 Wh/kg and the relatively low cost of sulfur. Thus, lithium-sulfur batteries can provide two to three times the energy density of today’s rechargeable lithium-ion batteries.1—3 However, the deployment of lithium-sulfur batteries has been limited by their relatively short cycle life.1—3 Practical cells have a cycle life of just 50–100 cycles. One of the major technical issues limiting the cycle life of the lithium-sulfur cell is the shuttling of soluble polysulfides between the two electrodes. In this article we demonstrate a new approach to suppressing the active shuttling of polysulfides in the lithium-sulfur battery by using a novel type of barrier layer. The novelty of this barrier layer lies in its ability to exclude the polysulfide ions while maintaining selectively the facile transport of lithium ions using a mixed conduction mechanism. We show that this type of barrier layer prevents capacity fade caused by the polysulfide shuttle and preserves the high discharge rate capability and energy density of the lithium-sulfur cell.

Overview of construction and operation of the lithium-sulfur cell.—In a lithium-sulfur battery the positive electrode is a sulfur-carbon composite supported on an aluminum foil or grid while the negative electrode is a foil of lithium metal.4—6 The positive and negative electrodes are separated by a thin porous sheet of polypropylene imbibed with an organic electrolyte. A lithium salt such as lithium bis(trifluoromethane)sulfonimide (LiTFSI) dissolved in a suitable organic solvent such a mixture of dioxolane and dimethoxyethane serves as the electrolyte. The electrochemical reactions that occur during charge and discharge of a lithium-sulfur battery are shown schematically in Figure 1.

During discharge, the lithium at the negative electrode dissolves into lithium ions, and sulfur at the positive electrode is converted to polysulfides. The higher-order polysulfides are then reduced in successive steps to the lower-order polysulfides until lithium sulfide (Li2S) is produced. During charging of the cell, the reverse process occurs, and lithium ions are re-deposited onto the negative electrode, and the sulfides are re-oxidized to higher-order polysulfides at the positive electrode. Although the positive electrode is assembled with elemental sulfur, after the first discharge and charge, the sulfur transforms to a solution of the higher-order polysulfides.

Polysulfide shuttle and previous efforts to suppress the shuttling process.—The higher-order polysulfides S82−, S62−, and S42− generated at the positive electrode are soluble in the electrolyte while Li2S2 and Li2S are insoluble in the electrolyte. Thus, the higher-order polysulfides can diffuse across the cell to the negative electrode. At the negative electrode, the higher-order polysulfides are reduced to the lower-order polysulfides either by reaction with metallic lithium or through electrochemical reduction during charging. Depending on the state of charge of the cell, the concentration of the different polysulfide species in the cell can vary. The polysulfides reduced at the lithium electrode then diffuse back to the positive electrode where

![Figure 1. Schematic of the electrochemical processes in a lithium-sulfur battery.](Image)

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they are re-oxidized again during charging. This shuttling of the polysulfides between the positive and negative electrode is a parasitic self-discharge process, widely referred to as the “polysulfide shuttle.” When the polysulfides are reduced to insoluble precipitates of lithium sulfide at the lithium electrode, the sulfur active material is irreversibly trapped and the lithium electrode begins to passivate. In addition to self-discharge, the polysulfide shuttle also reduces the cycle life, decreases the charging efficiency, and lowers the power output of the lithium-sulfur cell. Thus, preventing the polysulfides from reaching and reacting with the lithium electrode has been the focus of some of most recent research efforts in lithium-sulfur batteries. The previously proposed methods to stop the shuttling of polysulfides have met with varied levels of success. Among these methods are: (1) modification of the structure of the positive electrode to help retain the polysulfide, (2) modification of the electrolyte to alter the solubility of the polysulfides, (3) slowing down the diffusion of the polysulfide through the use of barrier layers, and (4) the use of electrolyte additives to form films that protect the lithium electrode from interacting with the polysulfides.

Modifications of the positive electrode have resulted typically in increased utilization and improved rate capability but the sequestered soluble polysulfide species eventually diffuse out of the electrode structure and contribute to the polysulfide shuttle. The use of barrier layers that slow down the diffusion of polysulfides may be effective when the cell is cycling at high rates. However, the polysulfides can still diffuse across the cell albeit slowly, and the cell performance decreases during slower rates of cycling or during idle stand. Thus, such porous barrier layers cannot prevent self-discharge and irreversible capacity losses. The use of a solid lithium ion conducting electrolyte layer can inhibit the polysulfide shuttle but at the expense of rate capability because of the typically poor lithium ion conductivity of conventional solid electrolytes. Lithium-ion conducting barrier coatings that protect the lithium electrode from contacting the liquid electrolyte also have the potential to be effective in suppressing the ill effects of the shuttle, but such protective layers tend to have poor chemical stability, low conductivity, and present challenges to the manufacturing of large capacity spirally-wound cells. Thus far, the most practical and effective method for avoiding the polysulfide shuttle has been the use of lithium nitrate as an additive to the electrolyte. Lithium nitrate is reduced on the surface of the lithium metal to form a passivation layer that prevents the soluble polysulfide species from reacting with the lithium metal surface. Lithium nitrate, however, is consumed in each cycle for the formation of this beneficial passivating film. Therefore, the beneficial effect of lithium nitrate is temporary. Thus, finding a durable solution for suppressing the polysulfide shuttle for the realization of a long-life lithium sulfur battery has remained a technical challenge.

Mixed Conduction Membrane Concept

To overcome the limitations presented by these previously proposed approaches we have designed a novel stable membrane layer that we term “Mixed Conduction Membrane” (MCM) that blocks the diffusion of soluble polysulfides from the sulfur cathode to the lithium anode while selectively allowing the facile transport of lithium ions (Figure 2). Such a non-porous MCM layer is sandwiched between two layers of a porous separator soaked with electrolyte, and this sandwich is in turn placed between the lithium anode and sulfur cathode. Therefore, deploying an MCM does not require any major modification to the rest of the cell including the electrodes or the electrolyte or the fabrication techniques. Unlike the lithium nitrate additive, the MCM is not consumed during cycling and remains an effective barrier to the transport of the polysulfides. Further, the approach uses readily available battery electrode materials that are compatible with the electrolyte and is scalable for manufacturing of lithium-sulfur cells of various types and sizes.

The MCM in Figure 2 has the following defining requirements: (1) is a non-porous structure (2) is a lithium ion conductor (3) is an electronic conductor and (4) presents an equilibrium potential for electrochemical lithium intercalation or insertion that is positive with respect to the fully-charged sulfur electrode (>-2.7 V vs. Li+/Li). A typical MCM material that meets these requirements would be a thin non-porous nanocomposite formed by combining lithiated cobalt oxide with a dense polymer binder such as polyvinylidene fluoride (PVDF). The MCM being non-porous does not allow the polysulfides to permeate the membrane layer. Thus, MCM can isolate the polysulfides to the positive electrode area, preventing the soluble polysulfides from reaching the negative electrode. Lithiated cobalt oxide is a well-known cathode material that undergoes facile intercalation and de-intercalation of lithium ions. The electronic conductivity of lithiated cobalt oxide is 1×10⁻²⁶ S cm⁻¹. The self-diffusion coefficient for fully lithiated cobalt oxide is in the range of 2×10⁻⁸ cm² s⁻¹. The electrochemical intercalation into the layered structure of lithiated cobalt oxide allows for the rapid diffusion of lithium ions. Thus, through a combination of intercalation reaction and diffusion, the lithium ions are transported through the membrane without impeding rate capability during charge and discharge.

Specifically, for a MCM made from lithiated cobalt oxide, ionic transport of lithium ions through occurs via the intercalation/de-intercalation reaction as shown in Eq. 1.

\[
\text{Li}_{1-y}\text{CoO}_2 + y\text{Li}^+ + y\text{e}^- \leftrightarrow \text{Li}_{1-y+y}^\text{+} \text{CoO}_2 \tag{1}
\]

Good electronic conductivity annuls the buildup of electric potential gradients arising from variations in concentration of lithium ions in the bulk of the membrane and assists with the rapid diffusion of lithium ions through the intercalation reaction pathway (Eq. 1). The electron conduction and ion conduction occur concomitantly, allowing such intercalation materials to conduct lithium ions effectively without change of chemical composition. Thus, during the conduction of lithium ions through the structure of lithiated cobalt oxide, there is no net change in the composition of lithium in the cobalt oxide matrix, although small changes could occur locally that would be rapidly equilibrated by electronic conduction and ion movement. Partially-lithiated cobalt oxide is even better suited for this function, as it has higher lithium-ion diffusivity compared to fully-lithiated cobalt oxide. Also, the partially lithiated structure is expected to facilitate lithium-ion injection and removal at a higher rate than the fully-lithiated cobalt oxide structure.

The positive electrode potential of the membrane prevents direct electrochemical reaction with the polysulfides and uncontrolled delithiation of the oxide material. The electrode potential of 4.2 to 3.1 V vs. Li⁺/Li of the partially lithiated cobalt oxide is positive to that
of the polysulfides that have an electrode potential in the range of 2.7 to 1.5 V vs. Li+/Li. The relative values of these electrode potentials ensure that the polysulfides do not react with the lithiated cobalt oxide. Reactions are precluded because the fully-lithiated cobalt oxide cannot be lithiated any further and the polysulfides are not readily oxidized beyond sulfur in non-aqueous electrolyte. Thus, the consideration of electrode potentials in the choice of materials for MCM is important to avoid undesirable chemical changes to MCM. Other intercalation cathode materials such as the lithiated nickel cobalt aluminum oxide (NCA), lithiated nickel manganese cobalt oxide (NMC), and lithiated manganese oxides (LMO) also meet this criterion of relative electrode potentials.

The MCM layer is electronically conducting and must be flanked by two electronically insulating layers of porous separator soaked with electrolyte. The separator layer could be the thin porous polypropylene material as the one commonly used in lithium batteries. This three-layer composite is then placed between the two electrodes of the lithium-sulfur cell (Figure 2). The electrically insulating layer of electrolyte and the separator are necessary to keep the MCM layer the decreased amount of sulfide deposition on the lithium electrode in cells using the MCM layer.

### Experimental

**Sulfur cathode fabrication.**—Sulfur (Aldrich, 99.5% purity), acetylene black (Alfa Aesar), and polyvinylidene fluoride (PVDF) binder (MTI) were mixed in with a composition of 60%, 30%, and 10% by weight, respectively, with N-methyl-2-pyrrolidone (NMP) solvent (Aldrich) to form a slurry. The slurry was coated onto an aluminum foil substrate using a doctor blade to a thickness of approximately 80 micrometers. The resulting electrode was dried under vacuum at 70°C for 8 hours and punched into disks of 16 mm in diameter. The total sulfur loading in the cathode was approximately 5.5 mg/cm².

**Fabrication of mixed conduction membrane layer.**—Lithiated cobalt oxide (MTI, molecular formula LiCoO2) and PVDF were mixed in with a composition of 95% and 5% by weight, respectively, with NMP to form a slurry. The slurry was coated onto a porous mixed conduction membrane layer. The total lithiated cobalt oxide loading was approximately 15.5 mg/cm². We designate this specific example of the MCM layer as the LCO membrane, as it is fabricated from lithiated cobalt oxide. The open area for permeation of the LCO membrane was determined to be less than 1% using a permeation cell setup. (Supporting experimental details and calculations are provided in the supplementary information section as Item 1.)

**Cell construction.**—Coin cells of the standard 2032 size were assembled using lithium foil (MTI) as the anode, polypropylene (Celgard 2400) as the porous separator, and with an electrolyte solution consisting of 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, Aldrich) in a 1:1 mixture (by volume) of dioxolane and dimethoxyethane (Aldrich). Cells were assembled with the MCM layer inserted between two polypropylene separators (Figure 2). Cells with 0.25 M lithium nitrate (Aldrich) additive in the electrolyte without the MCM layer were also assembled for comparative studies.

**Galvanostatic cycling.**—Coin cells were subjected to charge/discharge cycling under galvanostatic conditions using a battery test station (BST8-MA, MTI). Cell charging was cut off at 2.7 V while the discharging was terminated when the cell voltage reached 1.8 V. Cells were cycled at C/20, C/15, C/10, C/5, C/2 rates, where the nominal capacity, C, was calculated based on the amount of capacity achieved during initial cycling at a theoretical C/50 rate.

**Shuttle current measurements.**—Shuttle currents of coin cells were measured using a PAR VMC-4 potentiostat by a method de-
developed by us and published previously.45 Coin cells were cycled at C/20 rate for 5 cycles to ensure complete “formation” of the cathode as well as attainment of stable value of initial capacity before shuttle current measurements were started. The cells were then discharged to 2.30 V at the C/20 rate and held at that voltage for about 10 hours until steady-state currents were observed. This steady state current was recorded as the shuttle current. This process was repeated at 2.25, 2.20, 2.15, and 2.10 V with each cell type to determine the shuttle currents in the soluble discharge region of the sulfur electrode.

**Electrochemical impedance spectroscopy.**—The impedance of coin cells were measured in the frequency range of 0.01 Hz to 100,000 Hz using a PAR VMC-4 potentiostat and a sinusoidal excitation amplitude of ±2 mV (peak to peak).

**Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).**—The lithium electrodes were extracted from cells after two hundred cycles and imaged using a JEOL 6610 SEM. The EDX analysis was carried out on these electrodes afterwards using an iXRF EDX system.

**Results and Discussion**

**Shuttle currents.**—The shuttle current is a measure of the rate of transport of the polysulfide shuttle between the two electrodes. As mentioned earlier, we have developed a method to measure this type of current to quantify the effect of various cell modifications on the rate of polysulfide shuttling rate.45 We have used this shuttle current value as a direct measure of the transport rates of the polysulfide shuttle across the cell. In the present study, we have compared the shuttle current in three types of cells: (1) a cell with no membrane modification (2) a cell containing 0.25 M lithium nitrate additive and (3) a cell with the new MCM layer.

In a cell with no membrane, the polysulfide shuttle is operative at the maximum rate, especially near 100% state-of-charge where most of the polysulfides are present in a soluble form (Figure 5a). At lower states-of-charge, less soluble polysulfides appear and the shuttle current begins to decrease. For the cells with 0.25 M lithium nitrate additive and for the cells with the LCO membrane, the initial shuttle current was already 85% lower than that of cell without the membrane, and dropped to almost zero by 80% state-of-charge. The presence of shuttle currents at high states-of-charge for the cells with the LCO membrane is most likely due to the slight permeability that was measured for the fabricated membranes. (Supporting experimental details and calculations are provided in the supplementary information section as Item 1) The overall reduction in shuttle current with the lithium nitrate additive is not surprising as its role of suppressing the polysulfide shuttle is well known.39 However, a similar reduction in shuttle current observed with a LCO membrane suggests that the MCM layer is clearly effective in inhibiting the shuttle transport as much as the lithium nitrate additive.

Though both the lithium nitrate additive and MCM inhibit the polysulfide shuttle transport effectively, they do so by different means. Lithium nitrate forms a protective solid electrolyte interphase (SEI) on the lithium anode to prevent electrochemical reaction of the polysulfide at the lithium electrode.40–42 Since this protective layer has to be refreshed after every charge, the lithium nitrate additive is consumed in every cycle. The MCM, however, functions by physically excluding polysulfides from contacting the lithium anode altogether. Thus, the MCM layer can continue to perform its polysulfide blocking function cycle after cycle without being consumed unlike lithium nitrate. Consequently, a MCM barrier can provide a more lasting solution for blocking the polysulfide shuttle.

**Coulombic efficiency during charge-discharge cycling.**—In a lithium-sulfur cell, the reduction in Coulombic efficiency during charge and discharge cycling is a direct result of the parasitic self-discharge process caused by the polysulfide shuttle. In the case of the cell without a membrane, the polysulfides can freely diffuse between the electrodes. Therefore soluble polysulfides diffusing to the lithium anode are reduced, and these reduced polysulfides shuttle back to the sulfur cathode where they are reoxidized, resulting in the lower Coulombic efficiencies during charge and discharge. The Coulombic efficiency of the cell with MCM was 95%, while the cell without MCM had a Coulombic efficiency of 76% (Figure 5b). The higher Coulombic efficiency observed with MCM is equivalent to a 79% reduction in the polysulfide shuttle current.

**Deep-discharge cycling and cycling restricted to the soluble region.**—The lithium-sulfur cells cycled between 2.7 V and 1.8 V at the C/20 rate retained 69% of its initial capacity after 200 cycles when the LCO membrane was present, while the cell without the LCO membrane cycled under the same conditions only retained only 42% (Figure 6a). Thus a 50% lower rate of capacity fade is attributed to the benefit from blocking the polysulfide shuttle using LCO membrane. However, we note that although MCM was effective in blocking the polysulfide shuttle and reducing the capacity fade rate significantly, capacity losses were still observed in the cycling studies. This result suggested that other degradation mechanisms that are not linked with the rate of polysulfide shuttling still persist in these cells. Such additional mechanisms most likely arise from the gradual accumulation of insoluble products and passivation of the sulfur electrode that are not directly affected by MCM.46,47 However, these additional mechanisms are expected to be operative only when the cell is subject to deep discharge cycling in the region where insoluble lithium sulfide materials (Li2S and Li2S2) are produced. Thus, by avoiding
deep-discharge cycling and operating only in the region where soluble species are cycling, we may isolate the effect of the polysulfide shuttle and avoid confounding by the mechanisms of degradation arising from insoluble products or redistribution of materials at the cathode. The capacity fade measured under such conditions should be attributable to the effects of just the polysulfide shuttle. While all these mechanisms operate in concert in a conventional lithium-sulfur cell and are not separable, with the use of MCM we can separate the effect of the polysulfide shuttle separately.

Therefore, we set about to identify a protocol to cycle the cells in the soluble region by studying the effect of capacity on the rate of discharge. We observe that the discharge capacity output of a conventional lithium-sulfur cell cycled between 2.7 V and 1.8 V decreases with increasing rates of discharge (Figure 6b). The decrease in capacity output arises from a decrease of charge output from the plateau region of the voltage-time curve that is associated with the formation of insoluble discharge products. We must also note that cycling in the soluble region at high rates is possible only because of the mass-transport-controlled kinetics of oxidation and reduction of the soluble polysulfides. These rates are also dependent on the types of carbon used as the sulfur host matrix in the electrode. For electrodes using acetylene black as the carbon support, at very high rates such as C/2, the insoluble region does not contribute to the capacity; the discharge into the insoluble region is skipped over largely as suggested by the absence of a plateau in the discharge curve (Figure 6b). Consequently, by cycling at C/2 rate, we can restrict the cycling to the soluble region.

In the cycling studies conducted at C/2 rate, where the charge and discharge are inherently limited to only the soluble region, the cells with the LCO membrane experienced no measurable capacity fade even after 170 cycles (Figure 6c). A capacity increase is actually observed but since this cycling experiment utilizes a voltage cutoff to determine end of discharge, the increase in capacity is most likely caused by an increase in utilization due to a redistribution of active material upon cycling. The discharge profile (Figure 6d) showed that the cell with the LCO membrane continued to cycle in the soluble region even at the 170th cycle so the capacity increase observed stems from a greater utilization of soluble region rather than capacity accessed from the insoluble region. Conversely, the cells without MCM lost 40% of their initial capacity after 100 cycles and 80% after 170 cycles (Figure 6d). This result stands as proof to the claim that MCM was extremely effective in avoiding the capacity degradation from the shuffling of the soluble polysulfides.

**Electrochemical impedance spectroscopy.**—Impedance measurements indicate that the high-frequency resistance of the cell with the MCM layer are similar or even slightly lower than that for the cell without the membrane (Figure 7). The high-frequency resistance at 10 kHz was determined to be 19.04 Ω for the cell with the MCM layer and 14.31 Ω for the cell without the membrane using a standard Randles circuit fitting. (Supporting fitting data is provided in the supplementary information section as Item 2.) Since these impedance values are attributed to the ohmic transport processes, we may conclude that the ionic transport through MCM is not hindered relative to the cells without MCM. Alternately, we might say that lithium-ion conduction through MCM is as facile as in the liquid electrolyte. This conclusion is consistent with the behavior of lithiated cobalt oxide (the principal component of MCM) as a cathode offering high-rate capability in lithium ion cells. In this regard, we note that other solid-state lithium ion conductors that are not high-rate cathode materials can be expected to block the polysulfide shuttle but are likely to offer a higher resistance unless they can be made extremely thin. Thus, the MCM type barrier is unique in that it preserves the feature of high rate capability of the lithium-sulfur cell while providing the function of blocking the polysulfide shuttle.

At lower frequencies, the impedance is governed by the various faradaic and mass transport processes occurring at both electrodes. The faradaic impedance in the mid-frequency range of 10 kHz to 1 Hz appeared to be similar for the cells with and without the LCO membrane (Figure 7). However, a small increase in the impedance values is noted in the low frequency region that suggested that the diffusional
impedance at the interfaces of the electrodes are slightly increased with MCM. Such differences could be attributed to the unavoidable differences in compression of the cells with and without MCM. Also, the cells with MCM present two additional interfaces with the electrolyte that could contribute to the slightly higher impedance in the lower frequency region. However, these differences in impedance between the cells with and without MCM are quite small, consistent with the high discharge rates that can be sustained in cells with MCM.

Analysis of lithium electrodes after cycling.—After two hundred cycles, the coin cells were dis-assembled and the lithium electrodes were removed for physical analysis from cells of two types: (1) a cell with no membrane and (2) a cell with the MCM(LCO) layer. The scanning electron micrographs of the lithium electrodes show distinct differences. In particular, the lithium electrode from a cell with no membrane (Figure 8a) has a morphology with two differently shaded regions whereas the lithium electrode from a cell with the MCM layer (Figure 8d) has a more even morphology. Thus, incorporating the MCM layer dramatically influences the morphology of the lithium electrode. The MCM membrane was also found to be intact in the cells. An X-ray powder diffraction (XRD) analysis of the retrieved membranes found no compositional change in the membrane after two hundred cycles. (Supporting XRD data is provided in the supplementary information section as Item 3.) An energy dispersive X-ray (EDX) analysis of the lithium electrodes gave insight into the effectiveness of the MCM in suppressing the sulfide deposition reaction on the lithium surface due to the polysulfide shuttle. The EDX spectra of both the electrode from the cell with no membrane (Figure 8b) and from the cell with the MCM layer (Figure 8e) indicate the presence of sulfur, fluorine, carbon, and oxygen. For the purpose of this EDX study, sulfur and fluorine species were counted (Figure 8f) while carbon and oxygen species were excluded. The sulfur signal can originate from sulfide deposition due to the polysulfide shuttle as well as from the interaction of LiTFSI electrolyte with the surface of the lithium electrode. The fluorine signal however originates only from the LiTFSI electrolyte. For this reason, an EDX analysis of the LiTFSI electrolyte salt was also conducted (Figure 8c). Since the concentrations of sulfur and fluorine in the LiTFSI salt are coupled by being present within the same molecule, the ratio of the sulfur to fluorine count for the LiTFSI salt can serve as an internal standard. We measured the sulfur to fluorine ratio in LiTFSI by EDX to be 3.630.

In the EDX analysis the lithium electrode from the cell with no membrane the sulfur to fluorine ratio was 31.489 while for the electrode from the cell with the MCM layer the ratio was 7.062. If only LiTFSI was to be present at the surface of the lithium electrode, the sulfur to fluorine ratio should be about 3.630 as determined by us for the LiTFSI salt. Since the fluorine only comes from the TFSI salt and since all cells had the same amount of electrolyte added to the anode side, we can divide the ratios of the sulfur to fluorine to evaluate the excess sulfur present at the surface of the electrodes with and without the membrane. When we divide these ratios for the two types of cells, we find the cell without the membrane had a ratio of 31.489/3.63 = 8.674 while the cell with the membrane had a ratio of 7.062/3.63 = 1.94. Thus the MCM layer decreased sulfide deposition at the lithium electrode by almost 80%. However, the MCM layer still had a slightly higher sulfur to fluorine ratio than the baseline for the LiTFSI salt. Given the small permeability measured in the fabricated membranes, it is likely the polysulfide shuttling is not entirely suppressed, as observed in the shuttle current studies. This shuttling contributes to the elevated sulfur to fluorine ratio observed in the EDX analysis. Based on these results, we can expect that total suppression of the polysulfide shuttle will be possible with completely impermeable MCM layers.

Figure 7. Complex plane impedance plot of cells with and without the LCO membrane. Data at various frequency values ranging from 0.01 Hz to 100 kHz from right to left.

Figure 8. (a) SEM image and (b) EDX analysis of a lithium electrode from a cell using no membrane after two hundred cycles (c) EDX analysis of LiTFSI powder (d) SEM image and (e) EDX analysis of a lithium electrode from a cell using the LCO membrane after two hundred cycles (f) Table of Sulfur and Fluorine counts of the EDX analyses.
Conclusions

We have demonstrated that a mixed conduction membrane (MCM) incorporating a lithium-ion conductor such as lithiated cobalt oxide can be an effective barrier to the transport of the polysulfide ions across the electrodes of a lithium-sulfur cell. A lithium-sulfur cell with the MCM barrier does not suffer from the degradation processes resulting from the polysulfide shuttle. MCM is unique in that it is able to transport lithium ions with facility while blocking polysulfide transport. We are able to confirm that suppression of polysulfide transport by direct measurement of the shuttle currents. To be effective, the MCM must be fabricated with materials that undergo facile lithium intercalation or insertion reactions, allowing us to use many of the high-performance cathode materials already in use in lithium-ion batteries. By choosing a material that undergoes electrochemical lithium insertion in a potential range positive to that of the sulfur/polysulfide couples, any reaction of the polysulfides with the MCM can be avoided. By cycling the cells in the region where soluble polysulfides are present we demonstrate that capacity fade arising from the polysulfide shuttle can be avoided. The effect of MCM is comparable to that of using lithium nitrate additives, but the MCM membrane is expected to offer an extended benefit during cycling, as the MCM is not consumed in the cell unlike lithium nitrate. The internal resistance of the cell is largely unaffected by the presence of the MCM barrier. The MCM layer is easy to fabricate and can be incorporated readily using state-of-art manufacturing methods used in lithium ion batteries. One drawback to the approach is the need to have additional materials besides lithium and sulfur, and this could add to the cost of materials and reduce the energy density of the final device. The MCM layer designed in this study is a proof of concept that can be vastly improved upon by using other methods of fabrication such as spray or electrophoretic deposition for thinner MCM layers that use incorporating a lithium-ion conductor such as lithiated cobalt oxide.

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