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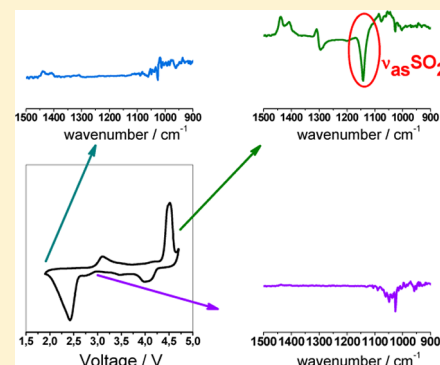
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Infrared Spectroscopy Studies on Stability of Dimethyl Sulfoxide for Application in a Li–Air Battery

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ABSTRACT: In situ infrared subtractive normalized Fourier transform infrared spectroscopy (SNIFTIRS) experiments performed simultaneously with the electroreduction of oxygen on gold and platinum cathodes in LiPF₆ dimethyl sulfoxide (DMSO) electrolyte have shown that the solvent is stable with respect to nucleophilic attack by the electrogenerated superoxide radical anion. However, long-term experiments with KO₂ solutions in DMSO have shown a slow formation of dimethyl sulfone. Evidence of dimethyl sulfone formation by anodic oxidation of DMSO above 4.2 V (Li/Li⁺) in the presence of trace water has been obtained on gold. On platinum, this unwanted reaction in the charging cycle of a lithium–air battery takes place at lower potentials, i.e., 3.5 V.



INTRODUCTION

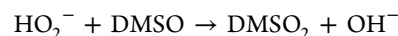
In recent years, Li–air battery technology has captured worldwide attention because of its high theoretical energy density that is 1 order of magnitude higher than that of Li–ion battery. It is believed to be a promising candidate to replace gasoline in electric vehicles.^{1,2} A nonaqueous rechargeable Li–air cell was first introduced in 1996 by Abraham,³ and it consisted of a Li metal anode, a nonaqueous polymer Li⁺ conducting electrolyte, and a porous carbon cathode. During discharge, oxygen from the air reduces to form lithium peroxide at the cathode, and the reverse reaction takes place while charging.

However, several challenges must be overcome before possible commercialization of the Li–air battery can be accomplished.^{4,5} During the discharge of the battery, the first oxygen reduction product is believed to be a superoxide anion O₂^{•−} that then disproportionates or undergoes further electrochemical reduction to form insoluble Li₂O₂.^{6–9} The stability of the electrolyte solvent against reactive reduced oxygen species is one of the main unsolved issues. It has been shown that various electrolytes, including those based on organic carbonates^{10,11} and organic ethers,^{12–14} undergo decomposition during the cycling of the Li–air battery.

Dimethyl sulfoxide (DMSO) was investigated as a possible aprotic solvent in lithium electrolyte for Li–air battery in 2010 by Laoire and co-workers; they demonstrated an increased stability of oxygen reduction species in this media.¹⁵ In 2012, several reports showed DMSO-based Li–air cells with promising electrochemical performance and also an increased stability of this electrolyte system with porous carbon¹¹ and gold¹⁶ cathodes. Also in 2013, Trahan et al.¹⁷ determined that DMSO is a practical solvent based on rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) cyclic voltammetry studies; they also reported a DMSO-based Li–

air cell with a carbon cathode. In a recent communication we have reported that soluble superoxide radical anions can be detected at a ring electrode of a RRDE system in lithium solutions of acetonitrile containing 0.1 M DMSO, unlike acetonitrile lithium electrolytes that show no evidence of soluble O₂^{•−}.¹⁸ It has been suggested that soluble superoxide can nucleophilically attack the solvent.

However, to date there is evidence of the stability of DMSO-based electrolytes for application in the Li–air battery. Further investigation is required because it has been reported before that DMSO in the presence of superoxide anions may undergo oxidation to dimethyl sulfone (DMSO₂). As early as 1968, Goolsby and Sawyer¹⁹ studied oxygen reduction reactions in DMSO on gold, platinum, and mercury electrodes. They reported that the electrochemical reduction of superoxide in DMSO in the presence of (C₂H₅)₄NClO₄ (tetraethyl ammonium perchlorate) produces dimethyl sulfone. This was concluded based on infrared data obtained during the large-scale reduction of oxygen at −2.05 V with evidence in the appearance of an IR peak at 8.81 μm (1135 cm^{−1}), which is characteristic of dimethyl sulfone. They suggested the following reaction:

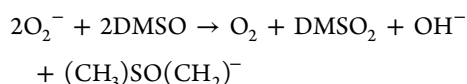


In 1982, Gampp and co-workers²⁰ reported superoxide first-order decomposition in DMSO with a half-life of 100 h to yield dimethyl sulfone, and sulfone was obtained after storage for two months at room temperature. The following decomposition mechanisms were suggested:

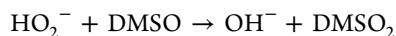
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or



In 1995, the anodic oxidation of DMSO in lithium perchlorate, fluoroborate, and potassium tetrafluorophosphate on Pt and glassy carbon electrodes were studied with in situ Fourier transform infrared (FTIR) spectroscopy in the presence of traces of water (strong absorption band in the 1100–1000 cm^{-1})²¹



In the present work, in situ infrared spectroscopy experiments were performed simultaneously with electrochemical experiments to investigate the DMSO-based electrolyte stability versus two Li–air cell discharge products, soluble superoxide anion and insoluble lithium peroxide, as well as anodic oxidation of DMSO, using Au and Pt as the cathode material. We performed the experiments in solutions of DMSO containing Li^+ salts and saturated in O_2 , in solutions of tetrabutylammonium (TBA^+) salts saturated in O_2 , and in deoxygenated solutions.

EXPERIMENTAL SECTION

Chemicals and Solutions. Anhydrous dimethyl sulfoxide, $\geq 99.9\%$ (276855 SIGMA-Aldrich), tetrabutylammonium hexafluorophosphate for electrochemical analysis, $\geq 99.0\%$ (86879 Fluka), lithium hexafluorophosphate battery grade, $\geq 99.99\%$ trace metals basis (450227 Aldrich), potassium dioxide (278904 Aldrich), lithium peroxide technical grade, 90% (347043 Aldrich) were purchased from Sigma Aldrich and stored in the argon-filled MBRAUN glovebox with an oxygen content ≤ 0.1 ppm and water content below 2 ppm. Dimethyl sulfoxide was dried for several days over 3 Å molecular sieves (208574 SIGMA-Aldrich); tetrabutylammonium hexafluorophosphate, lithium hexafluorophosphate, potassium dioxide, and lithium peroxide were used as received. All solutions were prepared inside the glovebox, and the water content was measured using the Karl Fisher 831 KF Coulometer (Metrohm). Solutions were found to contain around 50 ppm of water.

Electrochemical Experiments. Electrochemical experiments were performed in an airtight three-electrode cell. A nonaqueous Ag/Ag^+ reference electrode was prepared by placing a silver wire in a fritted glass compartment filled with a 0.01 AgNO_3 solution in acetonitrile (0.1 M tetrabutylammonium hexafluorophosphate was added to the solution to increase conductivity). The reference electrode was calibrated with respect to Li/Li^+ couple, which is commonly used as a reference in Li–air battery studies. Inside the argon glovebox, a Ag/Ag^+ electrode and a 3.2 mm diameter Li wire (99.9% trace metals basis, 220914 Aldrich) were placed in a beaker filled with 0.1 M LiPF_6 in DMSO, and the cell potential was measured with a high-impedance voltmeter, obtaining 3.7 V. It is worth mentioning that the potential measured between the same electrode and Li metal in a 0.1 M LiPF_6 solution in acetonitrile was 3.23 V, which is 0.47 V lower than that in

DMSO solution. This difference is explained by an important Li^+ solvation energy difference in DMSO and acetonitrile.

Infrared Experiments. Electrochemical in situ subtractively normalized interfacial fourier transform infrared spectroscopy (SNIFTIRS) experiments were carried out on a Thermo Nicolet 8700 (Nicolet, Madison, WI) spectrometer equipped with a custom-made external tabletop optical mount, an MCT-A detector, and a custom-made Teflon electro-chemical cell with a polycrystalline gold or platinum disc electrode aligned against the CaF_2 window, a 1 in. (25 mm) CaF_2 equilateral prism (Harrick Scientific Technology). Typically, a few micrometers of electrolyte solution separated the electrode and the CaF_2 window. The electrochemical cell was a conventional three-electrode cell connected to a Jaisle IMP88 Potentiostat controlled by the computer via a digital-to-analog converter (Agilent USB AD/DA converter). All potentials were measured with respect to a nonaqueous Ag^+/Ag reference electrode (as described above) and a Pt foil used as counter electrode. The electrode potential was varied from 3.0 to 2.0 V and back to 4.2 V in 0.05 V steps.

Each potential step comprises an equilibration time of 120 s followed by the acquisition of the spectrum by averaging 200 scans at 4 cm^{-1} resolution. For each system, a spectrum was obtained at open circuit and taken as reference.

In a typical in situ FTIR spectroscopy experiment, it is necessary to measure a reference spectrum at a potential, where the electrochemical process does not take place, and a sample spectrum, where the desired process does take place. A ratio of the two spectra is then obtained. This type of experiment was originally called subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS). In SNIFTIRS spectra, usually there are bands in both the up and down directions with respect to the baseline. Taking R_0 as the reflectance in the reference spectrum and R as the sample spectrum reflectance, positive bands ($R_0 > R$) correspond to consumption of species and negative bands ($R_0 < R$) correspond to appearance of new species.

Transmission spectra of the solutions were performed using a thin optical pass liquid cell with CaF_2 windows. The resolution was set to 4 cm^{-1} , and 200 scans were performed.

RESULTS AND DISCUSSION

IR Transmission Spectra of DMSO in the Presence of O_2^- and Li_2O_2 . A saturated solution of KO_2 in DMSO and a suspension of Li_2O_2 in DMSO (because lithium peroxide is insoluble in DMSO) were prepared. IR spectra of the prepared solutions were measured 24 h and 2 months after preparation. A spectrum of pure DMSO was also measured as a reference. The obtained spectra are shown in Figure 1. The spectrum of DMSO exhibits peaks at 1438, 1405, and 1310 cm^{-1} and a broad peak at around 1075 cm^{-1} . The peaks at wavenumber 1438 and 1405 cm^{-1} correspond to the antisymmetric bending of CH_3 ($\delta_{\text{as}}\text{CH}_3$), and the peak at 1310 cm^{-1} is identified as a symmetric deformation of CH_3 ($\delta_{\text{s}}\text{CH}_3$) group that is attached to the S atom. A broad peak around 1075 cm^{-1} can be assigned as $\text{S}=\text{O}$ stretching (νSO). The spectra of both solutions taken 24 h after the preparation are similar to the spectrum of pure DMSO. Furthermore, the spectrum of a mixture of DMSO and Li_2O_2 remains without noticeable changes after 2 months. On the other hand, the solution containing DMSO and KO_2 , after a 2 month period, exhibits an IR spectrum with new peaks at 1335, 1293, and 1142 cm^{-1} . A peak at 1142 cm^{-1} can be assigned to the symmetric stretching of SO_2 ($\nu_{\text{s}}\text{SO}_2$) and is a

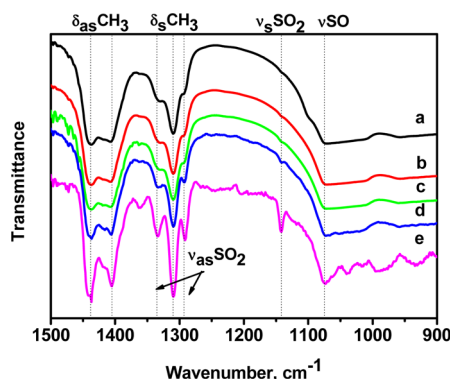


Figure 1. IR spectra of solutions: (a) pure DMSO; (b) DMSO with Li_2O_2 , measured 24 h after preparation; (c) DMSO with KO_2 , measured 24 h after preparation; (d) DMSO with Li_2O_2 , measured 2 months after preparation; (e) DMSO with KO_2 , measured 2 months after preparation.

characteristic peak of dimethyl sulfone (DMSO_2).^{22,23} The modes with wavenumbers of 1293 and 1335 cm^{-1} correspond to the asymmetric stretching of SO_2 group ($\nu_{\text{as}}\text{SO}_2$). Also, comparison of these spectra with standard spectra of DMSO and DMSO_2 ²⁴ makes it easy to identify that the obtained spectrum corresponds to a mixture of dimethyl sulfoxide and sulfone.

Therefore, we conclude that no significant changes in the DMSO solvent occur on short time scales (24 h) in the presence of superoxide anion or in the presence of lithium peroxide precipitate. But on long time scales, DMSO undergoes decomposition in the presence of superoxide anion to form dimethyl sulfone. However, in the presence of Li_2O_2 , no changes could be detected after a 2 month period.

It can be assumed that DMSO undergoes oxidation to DMSO_2 according to the following reaction:



It is hard to estimate the effect of this slow reaction on the rechargeability of the Li–air battery because the lifetime of superoxide anion is very short in the presence of Li^+ . To investigate this issue, spectroelectrochemical in situ IR experiments were performed using Au and Pt working electrodes.

In Situ IR Spectroscopy Results on Au. For the in situ SNIFTIRS experiment, a set of fixed potentials were applied to the cathode and the IR spectra were collected at each chosen potential in order to evaluate changes produced in the electrolyte.

Potentials were chosen according to the cyclic voltammetry (CV) data, performed in the O_2 saturated solutions of 0.1 M LiPF_6 in DMSO (Figure 2). For in situ IR experiments we chose potentials between 3.2 and 1.9 V on the forward scan (discharge) and between 3.0 and 4.8 V on the reverse scan (recharge). A potential of 3.2 V is about the open circuit potential of the Li–air battery where electrochemical reaction occurs according to the cyclic voltammetry results. At potentials between 2.8 and 1.9 V, reduction of O_2 to superoxide anion¹⁶ and its disproportionation to peroxide in the presence of Li^+ occur.⁶ In the potential range of the reverse CV scan, we have taken IR spectra at 3.0 and 3.8 V; those are potentials before

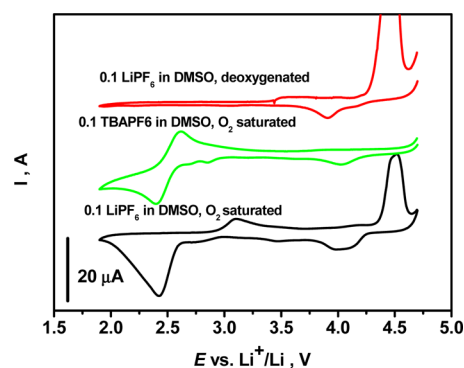


Figure 2. CV performed on Au electrode in the solutions of 0.1 M LiPF_6 in DMSO saturated in O_2 , 0.1 M LiPF_6 in DMSO deoxygenated, and 0.1 M TBAPF_6 in DMSO saturated in O_2 .

and after the oxidation peak of surface O_2 reduction product, LiO_2 and/or Li_2O_2 . At potentials between 4.2 and 4.8 V, the anodic oxidation of the solvent and possible oxidation of remaining surface O_2 reduction products occur.

The resulting IR spectra of experiments performed in a 0.1 M LiPF_6 solution in DMSO, saturated in O_2 on a Au electrode are presented in Figure 3. In the SNIFTIRS spectra, negative peaks (downward) correspond to the compounds that are formed. Positive peaks (upward) correspond to the modes that disappear. It is seen that on the forward scan at potentials between 3.2 and 1.9 V (discharge) and on the reverse scan at 3.0 and 3.8 V no changes in the IR spectrum, and thus in the composition of the solvent, occur near the electrode. However, during the recharge, application of potentials higher than 4.2 V results in clear detection of negative peaks at 1142 cm^{-1} (symmetric stretching vibration of SO_2 group) and 1295 cm^{-1} (asymmetric stretching vibration of SO_2 group). Note that the peak intensity increases with an increase in the anodic potential. These modes may be identified as a DMSO_2 formation and correspond to potentials where a clear anodic current is observed (Figure 2). Positive peaks at 1310, 1408, and 1438 cm^{-1} (Figure 3) are detected and can be assigned to the symmetric and asymmetric $\delta\text{-CH}_3$ bending vibration, corresponding to DMSO that is being consumed in the anodic process. At higher wavenumbers, we detect two downward peaks at 2920 and 3010 cm^{-1} and two upward peaks at 2910 and 2990 cm^{-1} . Those might be attributed to the shifting of symmetric and asymmetric C–H stretching vibrations while oxidizing DMSO to DMSO_2 . This is in a good agreement with standard spectra of DMSO and DMSO_2 . Also at the potentials higher than 4.2 V, a positive peak at around 3500 cm^{-1} is detected. That may be assigned to the O–H stretching and could be explained as depletion of trace water.

The same set of potentials have been applied in the in situ SNIFTIRS experiments of 0.1 M TBAPF_6 solution in DMSO saturated with O_2 and also in a deoxygenated 0.1 M LiPF_6 solution in DMSO to evaluate the possible differences in electrolyte decomposition in the absence of Li^+ cations and O_2 molecules. Current–potential curves measured in these solutions are shown in Figure 2.

SNIFTIRS results of a 0.1 M TBAPF_6 O_2 saturated solution in DMSO are depicted in Figure 4. No considerable differences can be noticed when compared to the IR spectra results obtained in O_2 saturated 0.1 M LiPF_6 solution in DMSO as described above. Identical results have been observed in oxygen free electrolyte (Figure 5).

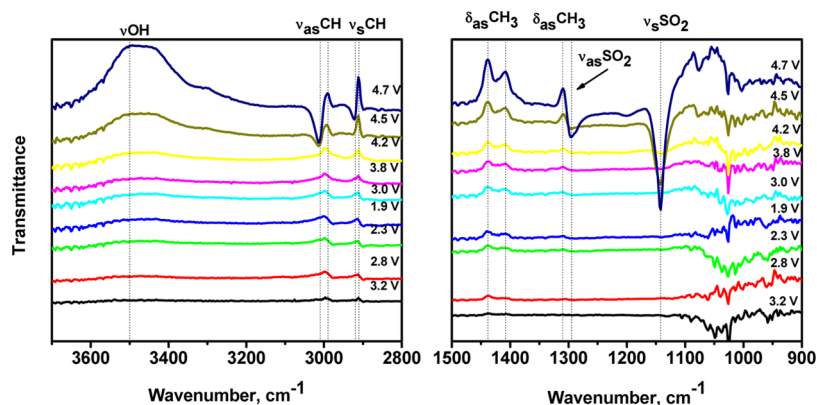


Figure 3. In situ IR spectra taken in a solution of 0.1 M LiPF₆ in DMSO, saturated in O₂ on a Au working electrode. Wavenumber ranges are 3700–2800 cm⁻¹ and 1500–900 cm⁻¹.

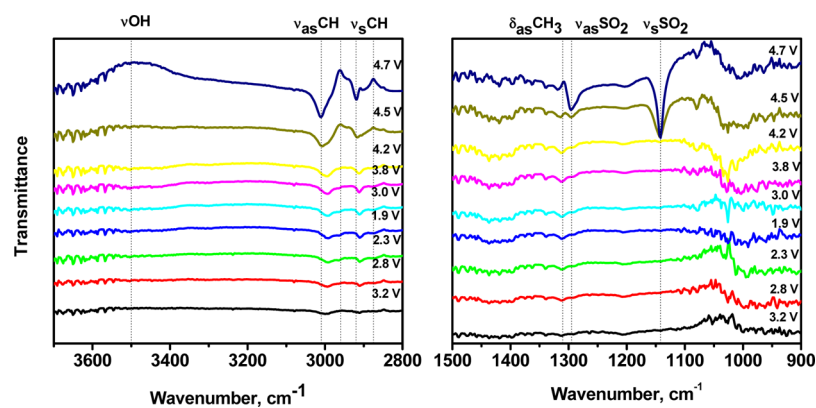


Figure 4. In situ IR spectra of a solution of 0.1 M TBAPF₆ in DMSO, saturated in O₂ on Au. Wavenumber ranges are 3700–2800 cm⁻¹ and 1500–900 cm⁻¹.

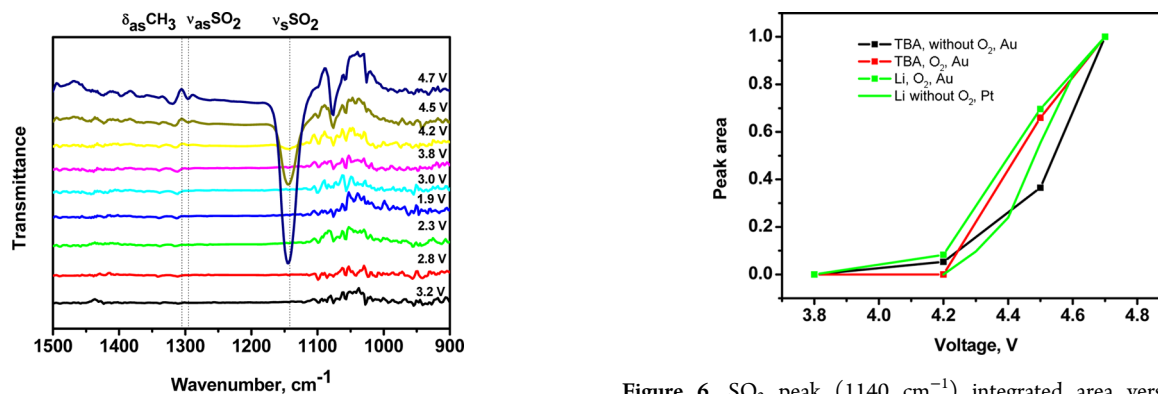


Figure 5. In situ IR spectra of a deoxygenated solution of 0.1 M TBAPF₆ in DMSO on Au.

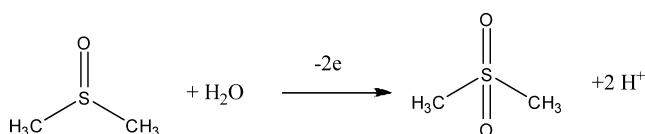
The normalized integrated peak area of SO₂ of dimethyl sulfone at 1140 cm⁻¹ versus applied potential is shown in Figure 6 for all three solutions. It can be seen that in all solutions decomposition of dimethyl sulfoxide to sulfone starts at around 4.2 V.

We conclude that at the potentials where O₂⁻ is formed, no appreciable electrolyte decomposition occurs in any of the studied solutions. This is consistent with the results previously reported for DMSO decomposition by O₂⁻ with a very low bimolecular rate constant ($k \sim 2 \times 10^{-6} \text{ M}^{-1} \text{ cm}^{-1}$).²⁰ Likewise, the solutions containing Li⁺ or TBA⁺ are stable in the presence of O₂⁻.

Figure 6. SO₂ peak (1140 cm⁻¹) integrated area versus applied potential of solution of 0.1 M LiPF₆ in DMSO, O₂ saturated, 0.1 M TBAPF₆ in DMSO, saturated in O₂ and deoxygenated, on a Au working electrode.

At potentials higher than 4.2 V, an anodic oxidation of DMSO is detected and the oxidation product can be easily determined as dimethyl sulfone. The same decomposition reaction was found to occur in both oxygenated and deoxygenated solutions. Therefore, we conclude that formation of dimethyl sulfone at high potentials is not a result of the presence of oxygen species in the solvent.

At the same potential where DMSO₂ is formed, depletion of traces of water has been detected, which indicates that DMSO oxidizes to DMSO₂ by reacting with traces of water. The suggested reaction is:



In Situ IR Spectroscopy Results on Pt. Cyclic voltammetry in O₂ saturated 0.1 LiPF₆ DMSO solution on Au and Pt working electrodes are shown in Figure 7. An

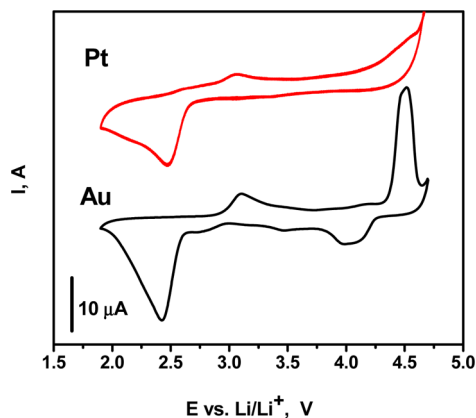


Figure 7. CV scans in a solution of O₂ saturated 0.1 M LiPF₆ in DMSO, on Pt and Au.

increase of the oxidation current is observed on the Pt electrode starting around 3.5 V; therefore, Pt catalyzes the parasitic reaction occurring during the oxidation (charging) reaction. In situ IR spectra have been recorded on the Pt electrode at potentials between 3.1 and 4.7 V (Figure 8).

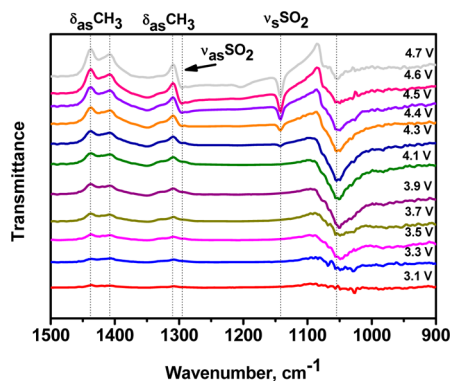
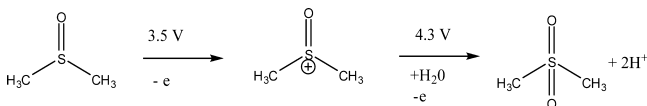


Figure 8. In situ IR spectra of a deoxygenated solution of 0.1 M LiPF₆ in DMSO, on Pt.

At 3.5 V, a peak at 1050 cm⁻¹ (S=O stretching) appears and increases in intensity with increasing potential; at 4.3 V, this peak starts to decrease, which coincides with the appearance of the 1150 cm⁻¹ mode characteristic of sulfone (similar to the evidence on the Au electrode). Unlike what occurred on Au, it is suggested that an intermediary of DMSO decomposition is formed on Pt which is subsequently oxidized above 4.3 V to form dimethyl sulfone, as shown by the 1150 cm⁻¹ mode. We speculate with the following mechanism:



This result implies that Pt catalyzes DMSO decomposition at lower potentials than Au, that is, from 3.5 V. Therefore platinum would not be a suitable catalyst to recharge a cell above 3.5 V for the DMSO-based Li–air cells.

CONCLUSIONS

We have studied the stability of the DMSO as a solvent in Li⁺ electrolyte for the Li–air battery. It has been found that in long time scales (2 month period), dimethyl sulfoxide undergoes chemical decomposition to dimethyl sulfone in the presence of superoxide anion, but no appreciable decomposition occurs in the presence of insoluble lithium peroxide. In situ SNIPTIRS experiments, however, have shown that DMSO is stable during electrochemical reduction of oxygen, but it undergoes electrochemical oxidation to dimethyl sulfone at high potential during charging of the battery. We have detected formation of dimethyl sulfone starting at 4.2 V on the gold electrode in O₂ saturated and deoxygenated LiPF₆ and TBAPF₆ solutions in DMSO. The Li–air cell should not be charged above 4.2 V with Au cathodes because of anodic electrolyte decomposition.

Concurrent with the formation of dimethyl sulfone, we have detected consumption of trace water from the solvent; thus, we conclude that water molecules react with DMSO to form DMSO₂ at high potentials. Therefore, water content in the electrolyte has to be carefully controlled.

Similar studies performed on Pt electrodes have shown electrolyte decomposition at a potential lower than that on Au electrodes. DMSO undergoes decomposition on Pt starting at 3.5 V with formation of an intermediate compound which then oxidizes further to dimethyl sulfone above 4.3 V.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

DMSO, dimethyl sulfoxide; DMSO₂, dimethyl sulfone; IR, infrared; FTIR, Fourier transform infrared; TBA⁺, tetrabutylammonium; SNIPTIRS, subtractively normalized interfacial fourier transform infrared spectroscopy; CV, cyclic voltammetry

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