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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

The Carbon Electrode in Nonaqueous Li−O_2 Cells

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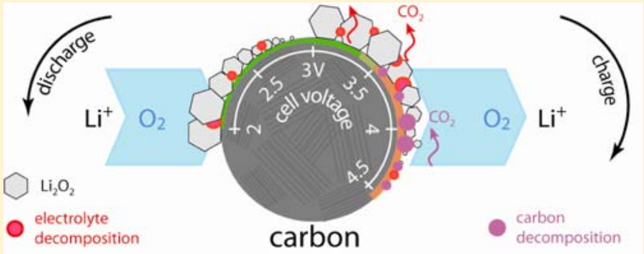
Supporting Information



ABSTRACT: Carbon has been used widely as the basis of porous cathodes for nonaqueous Li−O_2 cells. However, the stability of carbon and the effect of carbon on electrolyte decomposition in such cells are complex and depend on the hydrophobicity/hydrophilicity of the carbon surface. Analyzing carbon cathodes, cycled in Li−O_2 cells between 2 and 4 V, using acid treatment and Fenton's reagent, and combined with differential electrochemical mass spectrometry and FTIR, demonstrates the following: Carbon is relatively stable below 3.5 V (vs Li/Li^+) on discharge or charge, especially so for hydrophobic carbon, but is unstable on charging above 3.5 V (in the presence of Li_2O_2), oxidatively decomposing to form Li_2CO_3. Direct chemical reaction with Li_2O_2 accounts for only a small proportion of the total carbon decomposition on cycling. Carbon promotes electrolyte decomposition during discharge and charge in a Li−O_2 cell, giving rise to Li_2CO_3 and Li carboxylates (DMSO and tetraglyme electrolytes). The Li_2CO_3 and Li carboxylates present at the end of discharge and those that form on charge result in polarization on the subsequent charge. Li_2CO_3 (derived from carbon and from the electrolyte) as well as the Li carboxylates (derived from the electrolyte) decompose and form on charging. Oxidation of Li_2CO_3 on charging to ∼4 V is incomplete; Li_2CO_3 accumulates on cycling resulting in electrode passivation and capacity fading. Hydrophilic carbon is less stable and more catalytically active toward electrolyte decomposition than carbon with a hydrophobic surface. If the Li−O_2 cell could be charged at or below 3.5 V, then carbon may be relatively stable, however, its ability to promote electrolyte decomposition, presenting problems for its use in a practical Li−O_2 battery. The results emphasize that stable cycling of Li_2O_2 at the cathode in a Li−O_2 cell depends on the synergy between electrolyte and electrode; the stability of the electrode and the electrolyte cannot be considered in isolation.

■ INTRODUCTION

The high theoretical specific energy of the Li−air (O_2) cell has generated a great deal of interest in this energy storage device.[1−7] However, considerable challenges face the practical realization of a rechargeable Li−O_2 battery. Addressing such challenges requires a deeper understanding of the chemical/electrochemical processes that occur in the cell.

The reaction at the positive electrode in the nonaqueous (aprotic) Li−O_2 cell involves, on discharge, reduction of O_2 and formation of solid Li_2O_2; the process is reversed on charging, $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$.[1,8,9] The solid Li_2O_2 that forms on discharge must be stored in a porous conducting matrix, which in practice has to combine sufficiently high conductivity with low cost and ease of fabrication as a porous (three-dimensional) electrode. These requirements render carbon one of the most attractive materials for the fabrication of such an electrode. Stability of the conducting matrix during Li_2O_2 formation/decomposition on discharge/charge is also a vital requirement. Several recent reports have examined the stability of carbon cathodes in nonaqueous Li−O_2 cells.[10−13] In some reports the carbon electrode appeared relatively stable, whereas in others, side reactions were observed at the cathode and were attributed, either mainly or in part, to carbon decomposition.[10,12,13] However, it was unclear, in some cases, the extent to which decomposition occurred on discharge or charge.

Given the role of carbon as a possible porous positive electrode for nonaqueous Li−O_2 cells and the different observations reported in the literature, we undertook further investigation of the carbon electrode. In order to understand the behavior of the carbon electrode in a Li−O_2 cell, it is important to separate the decomposition processes that occurred on discharge from those on charge and to separate out the lithium carboxylates from Li_2CO_3; we describe here a procedure to do so. Also, ^{13}C carbon was employed to distinguish products originating from the carbon electrode from those arising from the electrolyte, as described previously.[10,12]

Our analysis shows that at the carbon electrode on discharge, whether in dimethyl sulphoxide (DMSO) or tetraethylene glycol dimethyl ether (tetraglyme) based electrolytes, the dominant product is Li_2O_2, and the dominant side reactions involve electrolyte rather than carbon decomposition. The major product of electrolyte decomposition is always Li_2CO_3, overwhelmingly so for carbon with a hydrophobic surface in contact with the DMSO electrolyte. For tetraglyme or hydrophilic carbon, the quantity of lithium carboxylates formed

Received: October 17, 2012
Published: November 28, 2012

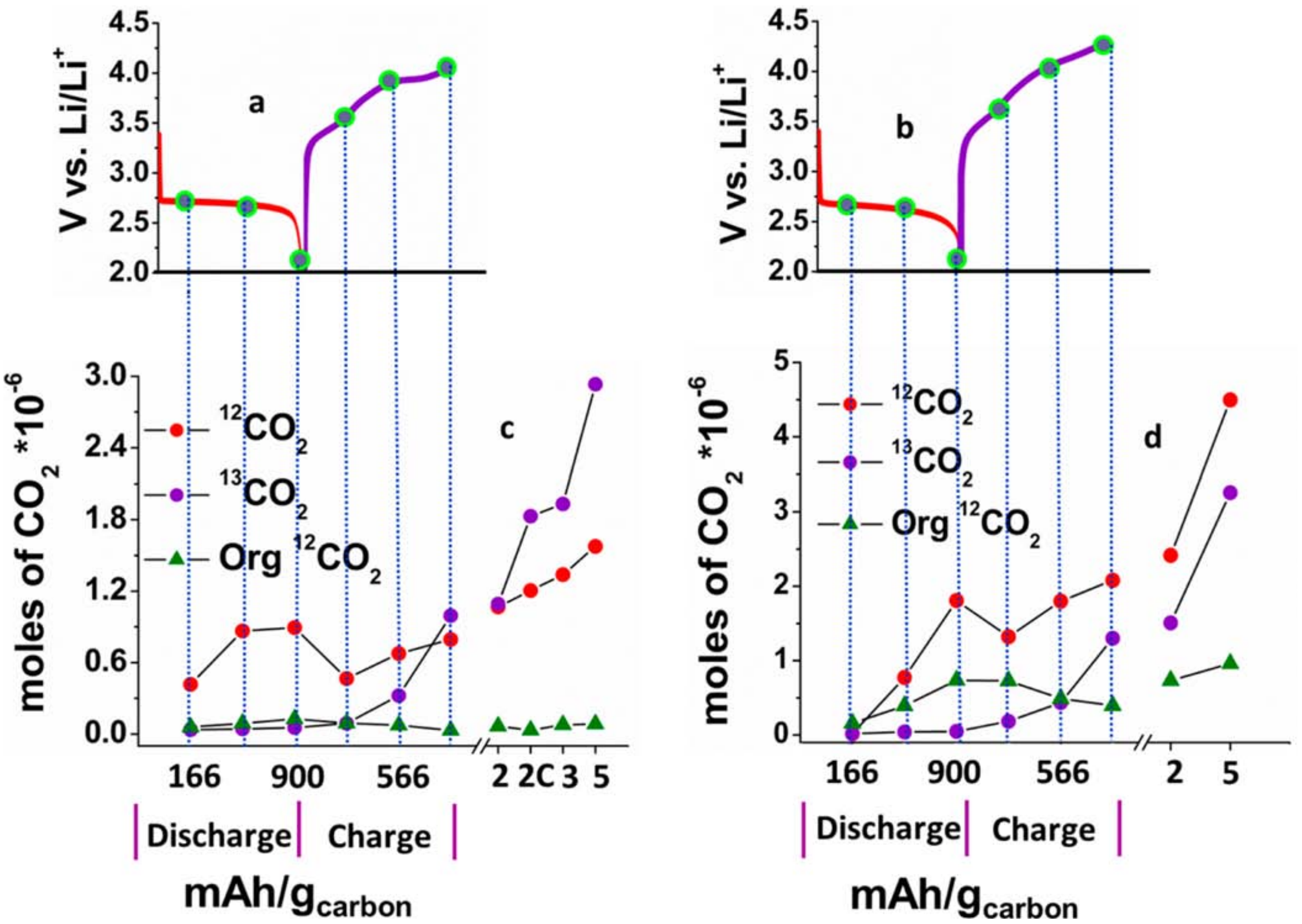


Figure 1. (a,b) Discharge−charge curves on the first cycle for DMSO- and tetraglyme-based electrolytes, respectively, at a carbon cathode; rate: 70 mA/g$_{carbon}$. (c,d) Moles of CO_2 evolved from the carbon cathodes, removed from the cells at the states of discharge and charge indicated by the green dots in (a,b), and then treated with acid to decompose $Li_2{}^{12}CO_3$ and $Li_2{}^{13}CO_3$ and Fenton's reagent to decompose the lithium carboxylates. The values (166 etc.) on the *x*-axis do not represent a scale but indicate the states-of-charge at which the cathodes were sampled. The numbers 2, 3, and 5 in (c) and 2 and 5 in (d) correspond to the electrodes analyzed at the end of discharge on those cycles, and the number 2C in (c) corresponds to the analysis of the carbon electrode at the end of the second charge.

more closely approaches that of Li_2CO_3. On subsequent charging up to ∼4 V, Li_2O_2, Li_2CO_3, and the lithium carboxylates are oxidized, while simultaneously more Li_2CO_3 and likely Li carboxylates are formed from electrolyte decomposition. Unlike discharge, during charge the carbon electrode exhibits significant decomposition above 3.5 V, to form Li_2CO_3, which simultaneously decomposes. On cycling between 2 and 4 V, there is a continuous accumulation of Li_2CO_3 arising from reactions involving the electrolyte and electrode which, as proposed previously by us and by others, results in electrode passivation and capacity fading in cells with carbon electrodes charged to 4 V.[10,13,14] However, the carbon electrode is relatively stable at ≤3.5 V. When DMSO is combined with a nanoporous gold electrode instead of carbon, the quantity of Li_2CO_3 formed is significantly less.[15] Also, the relative quantities of Li_2CO_3 and lithium carboxylates arising from the electrolyte differ according to the hydrophobicity of the carbon surface. Therefore, we propose that the carbon promotes electrolyte decomposition as well as decomposing directly to give rise to the formation of Li_2CO_3. This emphasizes that stable cycling of Li_2O_2 at the cathode in a Li−O_2 cell depends on the synergy between electrolyte and electrode; the stability of each cannot be considered in isolation.

■ RESULTS AND DISCUSSION

Nonaqueous Li−O_2 cells were constructed as described in detail in the experimental section (see Supporting Information). Two electrolytes were used, 0.5 M $LiClO_4$ in DMSO and 0.5 M $LiPF_6$ in tetraglyme. The DMSO-based electrolyte was chosen because it has been shown to exhibit good stability when cycled in Li−O_2 cells with nanoporous gold electrodes, and the tetraglyme electrolyte is among one of the more stable electrolytes, at least sufficiently so to permit investigation of the reactivity of the carbon electrodes.[14−18] The porous positive electrode was formed from ^{13}C carbon and PTFE, cast on a stainless steel grid. The cells were of Swagelok design and were operated in 1 atm of O_2. Cycling was carried out between 2 and 4/4.2 V for DMSO and tetraglyme, respectively, as this more than embraces the operating range of any practical Li−O_2 battery and is well within the stability limits of the electrolytes. The discharge−charge curves for each cell are shown in Figure 1a,b. In both cases discharge is dominated by a plateau at ∼2.65 V. Charging occurs in several steps, which have been attributed previously to the heterogeneous nature of porous electrodes

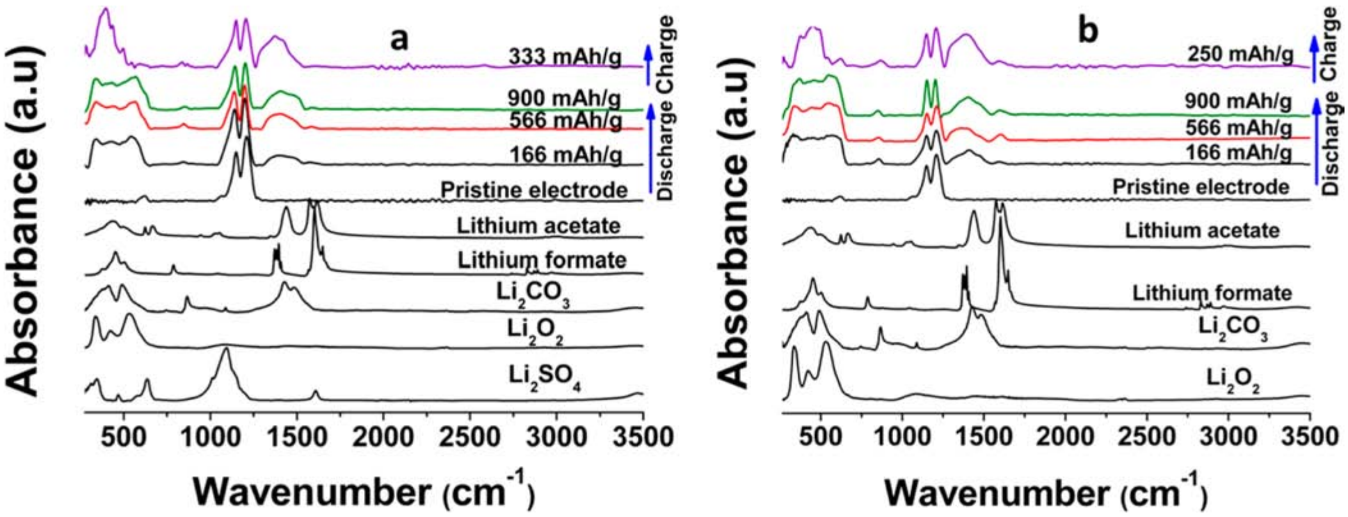


Figure 2. FTIR spectra of the carbon cathodes cycled in (a) DMSO and (b) tetraglyme electrolytes. Spectra at different states of discharge and then subsequent charge are shown. The peaks at 616, 1150, and 1206 cm^{-1} arise from PTFE.

and different morphologies/particle sizes of the discharge products exhibiting different degrees of polarization on oxidation.[11,19] Overall, the load curves are in good accord with many of those observed previously for the same electrolytes with carbon electrodes.[15−17,20−22] Cells were subjected to charging without prior discharge, to establish the anodic stability limit of the electrolyte/electrode, which was shown to be ~4.2 V in the case of DMSO and ~4.5 V in the case of tetraglyme (Figure S1). As a result, charging in DMSO was terminated at 4 V, whereas for tetraglyme a slightly higher cut-off potential of 4.2 V was used.

FTIR spectra were collected from the cathodes at different states of discharge then charge, on the first cycle, in DMSO and tetraglyme. These data, presented in Figure 2, confirm previous observations that the combination of DMSO or tetraglyme with carbon results in the formation of Li_2O_2, Li_2CO_3, HCO_2Li, and CH_3CO_2Li (lithium carboxylates) on discharge and that Li_2O_2 and the lithium carboxylates are oxidized on the subsequent charge.[14,15] As noted previously, it is not possible to identify separately HCO_2Li and CH_3CO_2Li by FTIR due to peak overlap, however, NMR, employed in the previous studies, demonstrated that both are present with carbon electrodes.[14,15] Therefore, we shall refer to these as lithium carboxylates.

In order to quantify the amounts of lithium carboxylates and Li_2CO_3 formed at each stage of discharge and charge and to identify the relative contributions of the electrode and the electrolyte to the side reactions that take place at the interface on discharge and charge, a new procedure was devised. It involves extracting the cathodes from the Li−O_2 cells at a different stage of discharge/charge, treating them with acid to decompose the Li_2CO_3 present in the electrode, followed by treatment with Fenton's reagent[23] to oxidize the lithium carboxylates (see the experimental section, Supporting Information). The CO_2 evolved in each case is determined by mass spectrometry. The CO_2 obtained on treatment with Fenton's reagent quantifies the amounts of lithium carboxylates that were present in the electrodes, whereas the $^{12}CO_2$ and $^{13}CO_2$ evolved on treatment with acid determine the amounts of Li_2CO_3 formed directly from the electrolyte and carbon electrode, respectively, since the ^{13}C isotopic species in the decomposition products can only arise from the carbon.

Each mole of Li_2CO_3 gives one mole of CO_2. The ratio for organic CO_2 depends on the exact amounts of formate and acetate. Also, in previous studies of tetraglyme at carbon electrodes, some other organic (polymeric) products were observed but could not be identified. However, the quantity was very small and was only observed for some carbons (Black Pearl).[14] Strictly speaking, the amount of organic CO_2 equates to the total amount of organic carbon in the decomposition products, so we do not rule out the possibility of other organic species contributing to the CO_2, but we refer to lithium carboxylates as these are the dominant organic compounds observed by FTIR/NMR. We also do not rule out the possibility of other inorganic carbonates contributing to the CO_2 evolved on acid treatment, although again we refer to Li_2CO_3 as this appears to be the main inorganic carbonate present. The results of the analysis carried out at different states of discharge and charge, as well as on cycling, are shown in Figure 1c,d for the DMSO and tetraglyme electrolytes, respectively. The as-received ^{13}C carbon has a hydrophobic surface, and its behavior is considered first. The influence of the hydrophobicity/hydrophilicity of the carbon surface on decomposition is discussed later. Three curves are shown in Figure 1c,d, corresponding to (i) the lithium carboxylates arising from the electrolyte (curve labeled org. $^{12}CO_2$); (ii) $Li_2{}^{12}CO_3$ arising from the electrolyte (curve labeled $^{12}CO_2$); and (iii) $Li_2{}^{13}CO_3$ arising from the carbon electrode (curve labeled $^{13}CO_2$). All of the data presented in Figure 1c,d are from identical electrodes, such that the quantities of CO_2 evolved from the decomposition of lithium carboxylates, $Li_2{}^{12}CO_3$ and $Li_2{}^{13}CO_3$, may be compared for a given state of charge and between one state of charge and another.

First Discharge. Considering the first discharge, there is very little decomposition of the carbon electrode; overwhelmingly, the side reactions involve decomposition of the electrolyte. For both electrolytes the dominant decomposition product is $Li_2{}^{12}CO_3$ on discharge, especially for DMSO, for which the quantity of lithium carboxylates is particularly low, compare Figure 1c,d. The quantity of $Li_2{}^{12}CO_3$ and lithium carboxylates increases with increasing depth of discharge. However, in the case of the DMSO-based electrolyte, the amount of $Li_2{}^{12}CO_3$ in the electrode at the end of discharge (2 V) is only marginally greater than that at the previous sampling point on the plateau (~2.65 V). This indicates that, although the amount of Li_2O_2 increases at deeper discharge, the quantity of $Li_2{}^{12}CO_3$ does not appear to do so. It may be that the lower potential (2 V) favors formation of Li_2O_2 over $Li_2{}^{12}CO_3$ in DMSO.

In the case of DMSO, electrolyte decomposition must also generate sulfur-containing compounds. None were observed by mass spectrometry or in solution by NMR, however careful examination of the FTIR spectra in Figure 2 reveals a shoulder on the peak at 1090 cm^{-1} which matches well the main band for Li_2SO_4. No other side reaction products were observed in solution or in the gas phase on discharge.

First Charge. Considering the subsequent charge, it is clear that even at 3.5 V, $Li_2{}^{12}CO_3$ formed from electrolyte decomposition on the previous discharge undergoes oxidation, Figure 1c,d. The amount of $Li_2{}^{12}CO_3$ in the electrode on charging at ~3.5 V is less than at the end of the previous discharge, i.e., some has decomposed. The ability to oxidize Li_2CO_3 below 4 V in Li−O_2 cells has been reported previously.[10,14,24] Li_2O_2 undergoes oxidation at and above 3 V; it is possible that Li_2O_2 (or its intermediates on oxidation) is involved in the mechanism of Li_2CO_3 decomposition, lowering the potential for Li_2CO_3 oxidation. As charging of the Li−O_2 cell proceeds to higher voltages, the quantity of $Li_2{}^{12}CO_3$ increases, i.e., $Li_2{}^{12}CO_3$ forms by electrolyte decomposition on charge as well as on discharge. In addition to the carbonate/carboxylate analysis, the behavior at the carbon electrode was probed by in situ differential electrochemical mass spectrometry (DEMS). The two methods are complementary, the acid/Fenton's analysis gives the amount of carbonates/organics in the cathode at each state-of-charge, whereas DEMS shows the gases evolved during the electrochemistry. Throughout the charging process continuous evolution of ${}^{12}CO_2$ was observed (Figure 3). Taken together, the data in Figure 1 and the in situ DEMS in Figure 3 show that, on charging, the electrolyte decomposes to form $Li_2{}^{12}CO_3$, and $Li_2{}^{12}CO_3$ is simultaneously being oxidized. Of course some of the ${}^{12}CO_2$ evolved on charging arises from decomposition of the lithium carboxylates; the amount of lithium carboxylates decreases as the charging voltage increases, see Figure 1c,d. Although the quantity of lithium carboxylates diminishes, we anticipate that they too are simultaneously formed and decomposed on charging. We do not rule out the possibility that in addition to $Li_2{}^{12}CO_3$ oxidation, there may be direct oxidation of the electrolyte to form ${}^{12}CO_2$. The electrolyte is stable under O_2 to 4/4.5 V for DMSO and tetraglyme, respectively, however it may decompose in the presence of Li_2O_2 or its intermediates on oxidation.[10]

Turning to the stability of the carbon electrode during charging, it begins to decompose above 3.5 V, forming $Li_2{}^{13}CO_3$ (Figure 1c,d and Figure 3). As in the case of $Li_2{}^{12}CO_3$, the quantity of $Li_2{}^{13}CO_3$ formed by decomposition of the carbon electrode increases with increasing charging voltage, at the same time ${}^{13}CO_2$ evolution in the in situ DEMS reveals that $Li_2{}^{13}CO_3$ is being oxidized (Figure 3). Therefore $Li_2{}^{13}CO_3$ is simultaneously being formed and partially oxidized on charging. As for the electrolyte, we do not rule out the possibility that alongside $Li_2{}^{13}CO_3$ oxidation, carbon may decompose directly to ${}^{13}CO_2$ in the presence of Li_2O_2 or its intermediates on oxidation. It does not do so when simply charged under O_2.

The plateau at ~3.5 V in the charging curve, Figure 1, is associated with Li_2O_2, $Li_2{}^{12}CO_3$ and Li carboxylate oxidation.

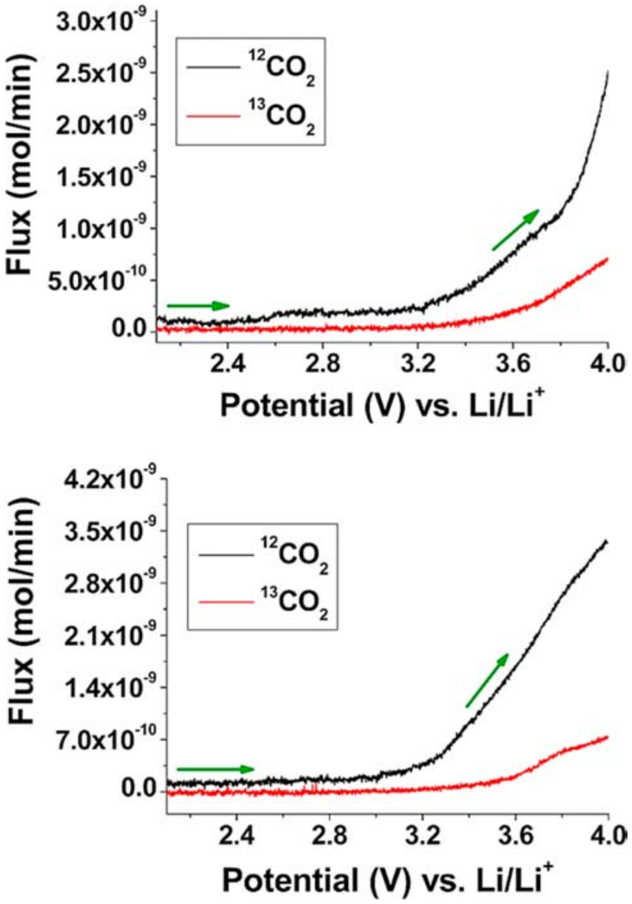


Figure 3. In situ DEMS data for CO_2 evolution from decomposition of products formed from the electrolyte (${}^{12}CO_2$) and the carbon cathode (${}^{13}CO_2$) in (a) DMSO- and (b) tetraglyme-based electrolyte; for the first charge after discharge to 2 V. Charging is carried out in an Ar:O_2 gas mixture (5:95 v/v).

Once carbon oxidation to $Li_2{}^{13}CO_3$ begins, Figure 3, the voltage soon rises to ~4 V, Figure 1, resulting in the high charging voltages required for Li−O_2 cells with carbon electrodes, which compromises energy/cycling efficiency and stability. It is noteworthy that at or below ~3.5 V, there is little evidence of carbon decomposition, therefore if Li_2O_2 oxidation were to be carried out at such low voltages, the carbon electrode may exhibit greater stability. The in situ DEMS also show minimal ${}^{13}CO_2$ at this voltage. However, carbon's ability to promote electrolyte decomposition to form Li_2CO^3 and Li carboxylates on discharge would remain a problem.

Cycling. On the second discharge, as on the first, the electrolyte decomposes to form lithium carboxylates and $Li_2{}^{12}CO_3$. As can be seen by comparing the quantity of ${}^{13}CO_2$ at the end of the first charge with that at the end of the second discharge, there is again little evidence of $Li_2{}^{13}CO_3$ formation (carbon decomposition) on discharge. On the second charge, the lithium carboxylates decompose. There is an increase in the quantity of Li_2CO_3 formed from decomposition of the electrolyte and the carbon electrode. Overall, the major trend on cycling to 4−4.2 V is continuous accumulation of Li_2CO_3. In the case of the DMSO-based electrolyte, the $Li_2{}^{13}CO_3$ arising from carbon decomposition soon becomes dominant, whereas for tetraglyme, the decomposition of the electrolyte continues to be a significant factor contributing to the accumulation of Li_2CO_3.

To ease comparison between the different electrolytes, CO_2 evolution from lithium carboxylates, $Li_2{}^{12}CO_3$ and $Li_2{}^{13}CO_3$, are presented separately in Figure 4. These plots show that on cycling, the tetraglyme based electrolyte gives rise to more CO_2 evolution for a given charge passed than DMSO. The amount of CO_2 is a measure of the number of carbon atoms in the decomposition products, which in turn is a measure of the number of carbon atoms lost from the electrolyte due to decomposition. In the context of a Li−O_2 battery, it is the proportion of electrolyte that decomposes for a given charge passed that is important in assessing electrolyte stability, and the number of carbon atoms lost is a useful measure of this (rather than the number of molecules). On this definition of stability, we conclude that tetraglyme is marginally less stable than DMSO, in accord with recent results.[14,15] We choose $LiPF_6$ as the salt for tetraglyme as it is widely used in lithium batteries. To ensure that it did not contribute to the greater decomposition of the tetraglyme, the experiment was repeated with LiTFSI, Figure S2. The results for $LiPF_6$ and LiTFSI are almost identical. Formation of lithium carboxylates are especially low for DMSO. Figure 4 also makes it very clear that decomposition of the carbon electrode is almost identical for the two electrolytes. Therefore, regardless of the stability of the electrolyte, a carbon electrode will decompose to form Li_2CO_3, when used in a nonaqueous Li−O_2 cell and cycled above ~3.5 V. The Li_2CO_3 is not completely oxidized and hence accumulates on cycling leading to electrode passivation and capacity fading.

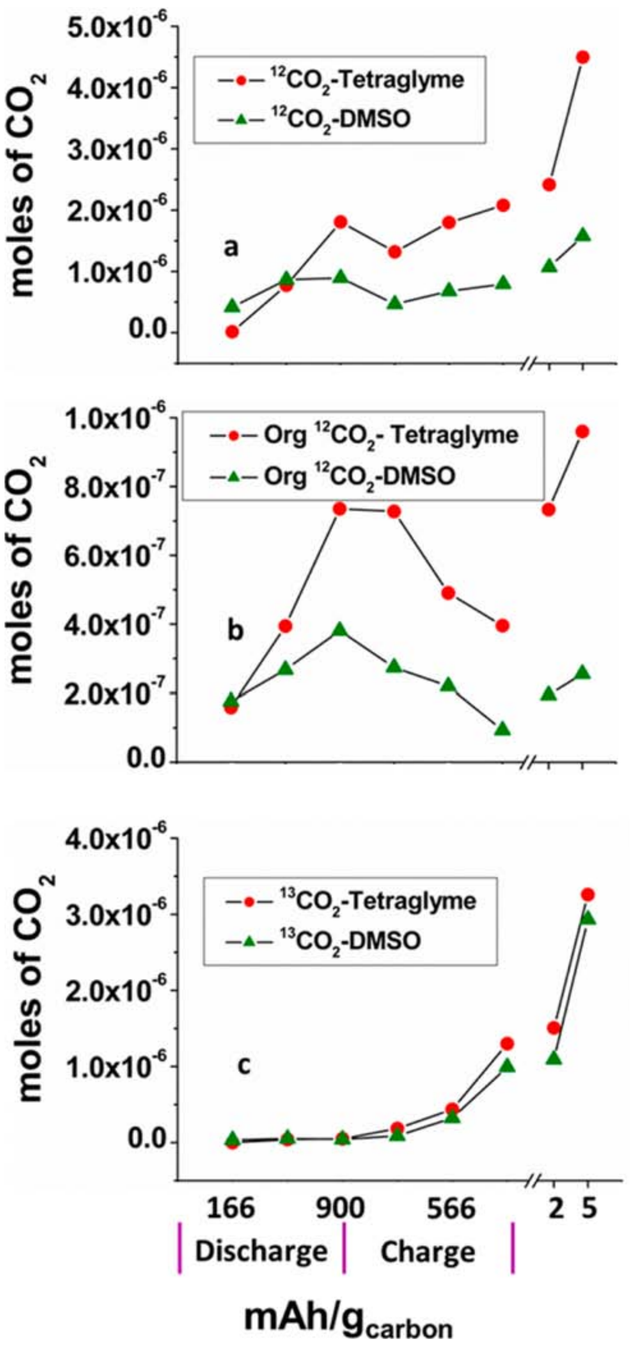


Figure 4. Direct comparison of the CO_2 evolution from decomposition of (a) $Li_2{}^{12}CO_3$ (formed from decomposition of the electrolyte), (b) lithium carboxylates, and (c) $Li_2{}^{13}CO_3$ (formed from decomposition of the carbon cathode) when cycled in 0.5 M $LiClO_4$ in DMSO and 0.5 M $LiPF_6$ in tetraglyme. The numbers 2 and 5 correspond to data collected at the end of the second and fifth discharge, respectively.

The masses of $Li_2{}^{12}CO_3$ and $Li_2{}^{13}CO_3$ present in the carbon electrode at the end of each discharge, expressed as a percentage of the amount of Li_2O_2 present, are shown in Figure 5 for the DMSO electrolyte. During cycling, both increase, but carbon decomposition becomes dominant over electrolyte decomposition, as noted above, to reach 10% of the product in the electrode after five cycles. As noted above, in the present study we confined charging to 4/4.2 V to stay well within the oxidation stability of the electrolytes and as this is higher than a practical Li−O_2 cell is likely to experience. In our earlier studies of glymes we charged the cells to 4.6 V at a carbon electrode, and there was no evidence of Li_2CO_3 at the end of the first charge, in contrast to the results here, demonstrating that charging to these higher potential results in greater Li_2CO_3 oxidation.[14] It is the formation of Li_2CO_3 that results in the large charging polarization and hence need to use such high potentials to obtain cycling. However, after five cycles even with a 4.6 V cutoff, Li_2CO_3 was observed at the end of charge. Hence charging to higher voltages delays but does not eliminate passivation and capacity fading/cell failure.

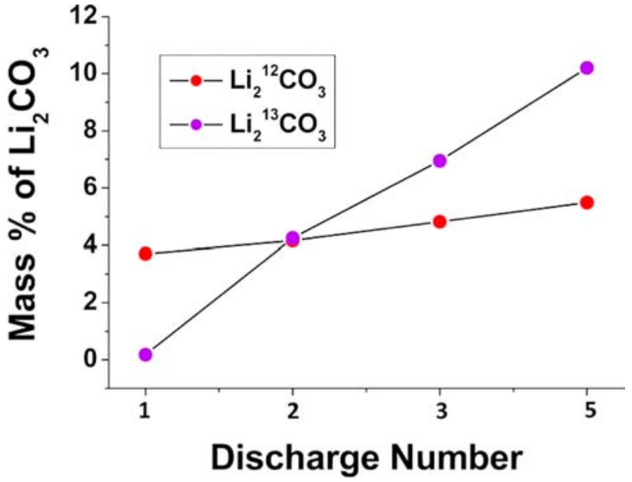


Figure 5. Amounts of Li_2CO_3 formed from the carbon cathode ($Li_2{}^{13}CO_3$) and the electrolyte ($Li_2{}^{12}CO_3$) at the end of each discharge in 0.5 M $LiClO_4$/DMSO expressed as a percentage of the Li_2O_2 in the electrode.

Hydrophobic/Hydrophilic Carbon. The surface of carbon can vary between the extremes of hydrophobicity and hydrophilicity. To investigate the influence of the surface polarity on the reactivity of the carbon, the ^{13}C powder was treated with 5 M HNO_3 under refluxing conditions overnight to form a hydrophilic surface, and a separate batch was heated in an Ar:H_2 mixture at 900 °C to form a hydrophobic surface, as described in more detail in the experimental section (see Supporting Information). Li−O_2 cells with the DMSO based electrolyte were constructed using the different carbon electrodes and were subjected to discharge then charge and analyzed as described for the as-received carbon. The results are presented in Figure 6. The data for untreated and hydrophobic carbons are very similar, showing that the as-received carbon was hydrophobic. In contrast, the behavior of the hydrophilic carbon is somewhat different. The quantity of $^{12}CO_2$ derived from the lithium carboxylates is ∼6-fold greater for hydrophilic carbon, Figure 6a, demonstrating that there is greater electrolyte decomposition. We speculate that this is due to a higher density of C−O, COOH, and C−OH groups on the carbon surface.[25,26] The quantity of $Li_2{}^{12}CO_3$ formed by electrolyte decomposition on discharge, Figure 6b, is similar for hydrophobic and hydrophilic carbon electrodes, however, in the case of the hydrophilic carbon, instead of increasing in quantity during charge, it decreases. Finally, the extent to which the carbon electrode decomposes is greater for hydrophilic carbon, as shown in Figure 6c; now some carbon decomposition on the first discharge is apparent. Overall, hydrophobic carbon is more stable than its hydrophilic counterpart; the latter exhibiting greater decomposition and promoting more decomposition of the electrolyte.

Electrolyte decomposition involves Li_2O_2 or its intermediates (LiO_2, O_2^-); it does not occur on charging the cell under O_2 in the absence of Li_2O_2. The stability of the electrolyte depends on the hydrophilicity/hydrophobicity of the carbon surface. Also, if the DMSO electrolyte is combined with a nanoporous gold electrode instead of carbon, there is much less electrolyte decomposition. Li_2CO_3 accounts for <0.5% of the product at the end of discharge for nanoporous gold (Figure S3) compared with 4% for carbon, and this value rises on cycling with a carbon electrode, whereas it remains the same for nanoporous gold.[15] The sensitivity of electrolyte decomposition to hydrophobicity/hydrophilicity of the carbon surface and the major suppression of decomposition with nanoporous gold demonstrate that the carbon electrode promotes decomposition of the electrolyte on discharge and charge.

Carbon Instability. The major contribution to carbon decomposition on cycling occurs on charging above 3.5 V. There is no evidence of carbon decomposition on charging a cell up to 4 V under O_2, before discharge (Figure S4). Equally, a purely chemical reaction between carbon and Li_2O_2 is not sufficient, even though thermodynamically favorable, to explain the relatively extensive carbon decomposition on oxidation; otherwise extensive decomposition would occur in the presence of Li_2O_2 below 3.5 V, which it does not. To investigate further the direct reactivity of carbon with Li_2O_2, carbon was mixed with Li_2O_2 (the quantity of Li_2O_2 being equivalent to 1000 mAh/g of carbon), only a very small amount of the carbon, corresponding to 0.1% of a monolayer on the carbon surface, decomposed to form $Li_2{}^{13}CO_3$ (determined by the carbonate/carboxylate analysis) see Figure S5. This result is in good agreement with the small amount of $Li_2{}^{13}CO_3$ observed in Figure 5 at the end of the first discharge, suggesting that direct reaction between Li_2O_2 and carbon may be responsible for the small quantity of $Li_2{}^{13}CO_3$ on discharge, as suggested previously.[10] The carbon decomposition on charge only occurs above 3.5 V and in the presence of Li_2O_2 oxidation. It does not occur at lower voltages even though Li_2O_2 is being oxidized, demonstrating that Li_2O_2 or its intermediates as well as a sufficiently high oxidizing potential are required for carbon decomposition to Li_2CO_3.[27,28] There is an interesting parallel between the ability of H_2O_2 to promote carbon oxidation in aqueous electrolytes at lower voltages that is otherwise possible and the ability of Li_2O_2 to promote carbon oxidation here. It is

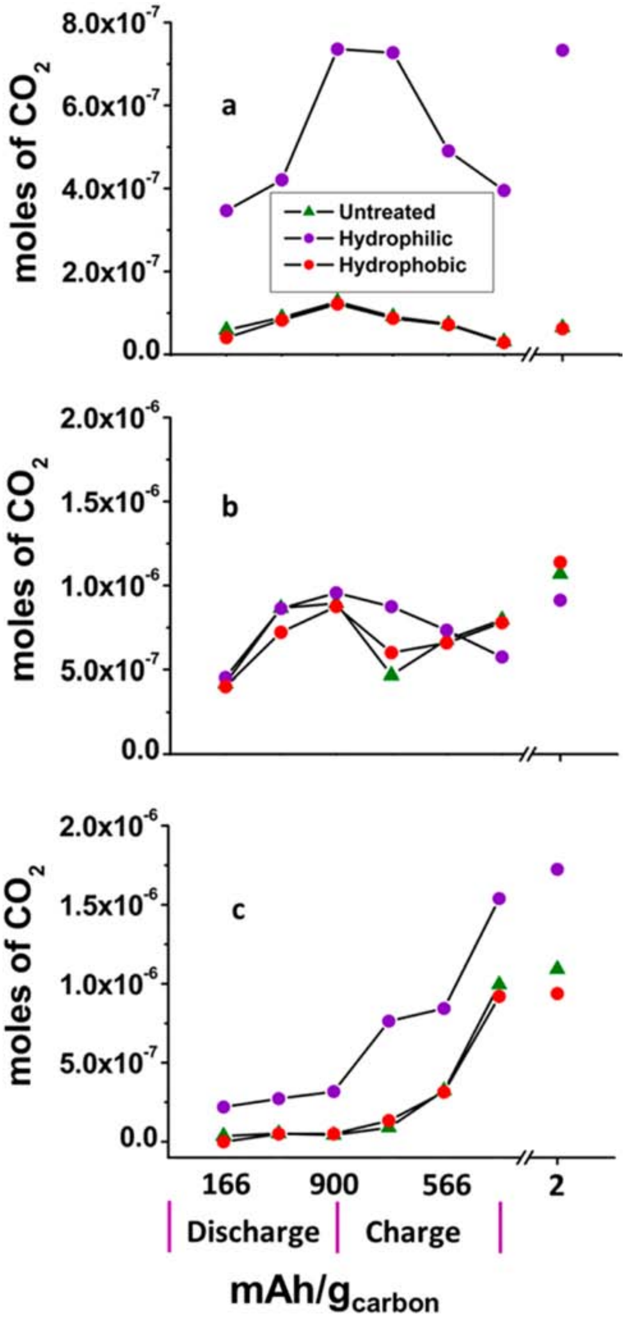


Figure 6. Comparison of hydrophilic, hydrophobic, and as-received carbons, demonstrating the effect of carbon surface polarity on the decomposition products. (a) $^{12}CO_2$ from Li carboxylates, (b) $^{12}CO_2$ from $Li_2{}^{12}CO_3$ formed from electrolyte decomposition, and (c) $^{13}CO_2$ from $Li_2{}^{13}CO_3$ formed from electrode decomposition. The number two corresponds to the data collected at the end of second discharge.

not surprising that hydrophilic carbon, with its more polar surface (including surface groups such as C−O, COOH, C−OH) is more reactive toward strong nucleophiles, such as LiO_2.

CONCLUSIONS

The behavior of the carbon electrode in a nonaqueous Li−O_2 cell is complex. It depends on the hydrophobicity/hydrophilicity of the carbon surface and involves potential dependent carbon decomposition and electrolyte decomposition promoted by the carbon surface. The results demonstrate the power of combining a new procedure for analyzing the products in the electrode using acid treatment and Fenton's reagent, along with FTIR and in situ DEMS. Applying these methods to a Li−O_2 cell with a carbon electrode in DMSO- and tetraglyme-based electrolytes, demonstrates that the following occurs during cycling between 2 and 4 V (a range that more than embraces any practical Li−O_2 cell): On discharge there is little or no decomposition of the carbon if hydrophobic; some decomposition does occur for hydrophilic carbon. The product in both cases is Li_2CO_3. The dominant side reactions on discharge involve electrolyte decomposition to form mainly Li_2CO_3 accompanied by lithium carboxylates (HCO_2Li and CH_3CO_2Li). On the subsequent charge up to ∼4 V, Li_2CO_3 and the lithium carboxylates undergo oxidative decomposition as, simultaneously, more forms by decomposition of the electrolyte. The carbon electrode decomposes above 3.5 V to also form Li_2CO_3, which again simultaneously undergoes oxidative decomposition. The net effect is that the formation of Li_2CO_3 from electrolyte and electrode exceeds Li_2CO_3 decomposition, and hence Li_2CO_3 accumulates in the electrode, leading to rapid polarization on charging as well as electrode passivation and capacity fading on cycling, as described previously.[10,13,14] Hydrophobic carbon is more stable and less able to promote electrolyte decomposition than its hydrophilic counterpart. The DMSO-based electrolyte is somewhat more stable than tetraglyme. As the major contribution to carbon decomposition occurs on charging above 3.5 V, direct chemical reaction with Li_2O_2 is not primarily responsible for this carbon decomposition. Carbon decomposition on charging occurs during Li_2O_2 oxidation, suggesting the mechanism of carbon decomposition to form Li_2CO_3 involves reaction with an intermediate, such as LiO_2. As carbon decomposition is much less at or below 3.5 V, if charging of Li_2O_2 could be carried out at a carbon electrode below 3.5 V, carbon may be a suitable electrode, although the formation of Li_2CO_3 on discharge and its ability to promote decomposition of the electrolyte may still prove problematical. The results emphasize that stable cycling of Li_2O_2 at the cathode in a Li−O_2 cell depends on the interplay between the electrode and the electrolyte rather than each in isolation.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P.G.B. is indebted to the EPSRC and Alistore for financial support.

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