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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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On the Efficacy of Electrocatalysis in Nonaqueous Li−O_2 Batteries

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S Supporting Information

ABSTRACT: Heterogeneous electrocatalysis has become a focal point in rechargeable Li−air battery research to reduce overpotentials in both the oxygen reduction (discharge) and especially oxygen evolution (charge) reactions. In this study, we show that past reports of traditional cathode electrocatalysis in nonaqueous Li−O_2 batteries were indeed true, but that gas evolution related to electrolyte solvent decomposition was the dominant process being catalyzed. In dimethoxyethane, where Li_2O_2 formation is the dominant product of the electrochemistry, no catalytic activity (compared to pure carbon) is observed using the same (Au, Pt, MnO_2) nanoparticles. Nevertheless, the onset potential of oxygen evolution is only slightly higher than the open circuit potential of the cell, indicating conventional oxygen evolution electrocatalysis may be unnecessary.

As a result of their high theoretical specific energy, rechargeable Li−air batteries have recently attracted considerable attention as possible energy storage devices for electric vehicles and other high energy applications. However, numerous scientific challenges still need to be overcome to enable practical high capacity rechargeable Li−air batteries.[1] Nonaqueous aprotic Li−air batteries are based on the net electrochemical reaction $2(Li^+ + e^-) + O_2 \leftrightarrow Li_2O_2$ with a thermodynamic potential $U_0 = 2.96$ V from the Nernst equation. Early Li−O_2 experiments exhibited modest overpotential for discharge (∼0.3 V) but very high overpotentials (∼1−1.5 V) for charging.[2,3] These overpotentials result in a large energy storage inefficiency (much more energy is required to charge the battery than is released during discharge).

Several authors have suggested the use of either metal oxide or metal nanoparticles as electrocatalysts in the cathode to reduce the overpotentials, especially for charging.[2,4−6] Li−O_2 discharge−charge cycles in cells employing carbonate or mixed ether−carbonate based electrolytes do in fact show considerable electrocatalytic reduction of the overpotentials when metal or metal oxide nanoparticles are added to the cell cathode.[4,6] Published Li−O_2 oxygen evolution reaction (OER) catalysis studies to date were performed using carbonate-based solvents, which are known to decompose on cell discharge.[7−9] None have yet been published using pure ether or other solvents in which Li_2O_2 formation is the dominant discharge product. Furthermore, we are unaware of any studies that have coupled coulometry (i.e., constant current discharge−charge cycles, cyclic voltammetry, etc.) and gas consumption and evolution data to elucidate the cathode catalysts' role in fundamental Li−O_2 electrochemistry.

This study employs quantitative differential electrochemical mass spectrometry (DEMS) to complement coulometry when studying cells with various added cathode nanocatalysts. Our results indicate that in Li−O_2 cells employing dimethoxyethane (DME) as a solvent, where Li_2O_2 is the dominant discharge product, metal (platinum and gold supported on Vulcan XC72 carbon) and metal oxide (α-MnO_2 nanowires mixed into XC72 carbon) catalysts do not lower the oxygen evolution reaction (OER) potential compared to pure carbon. Furthermore, the onset potential at which oxygen evolution occurs (as measured using an oxidative linear potential scan) is nearly identical for all cathodes and is just above the open circuit voltage of the discharged cell (∼2.8 V). We suggest that the experimental signatures that earlier reports attributed to effective OER catalysis are actually indicative of electrocatalysis related to electrolyte solvent decomposition. The use of platinum as a catalyst has a particularly large effect on electrolyte decomposition with all solvents.

We first explored solvent systems similar to those used in earlier OER electrocatalysis studies.[5,10] The cell cathodes were also similar to those used by other researchers. Figure 1 shows the first discharge−charge cycle for cells employing a propylene carbonate (PC)−dimethoxyethane (DME)-based solvent. When comparing the traces in Figure 1a, inclusion of cathode catalytic particles results in a significant reduction in charge voltage compared to the cell employing a carbon-only (XC72) cathode. Platinum and gold also increase the cell voltage during discharge. These results agree with similar studies published previously.[5,10]

However, Figures 1b and c show that CO_2 is predominantly evolved from all cells during charge, with only a small amount of O_2 evolution during the initial stages of cell charging. Carbonate decomposition has been previously identified as the primary electrochemical reaction during discharge. This decomposition leads to lithium alkyl carbonate electrodeposits on the cathode that evolve CO_2 upon cell charge.[8,9] Presumably, the lowering of the cell potential during charging is due to catalysis of CO_2 evolution from soluble mobile intermediates that are formed during the complex Li−O_2 discharge and charge electrochemistry.

Clearly, the inclusion of cathode catalyst particles results in the lowering of the overpotential for CO_2 evolution from carbonate decomposition products. However, O_2 evolution in these cells corresponds to the small voltage plateau observed at ∼3.15−3.2 V.

Received: August 1, 2011
Published: October 13, 2011

dx.doi.org/10.1021/ja207229n | *J. Am. Chem. Soc.* 2011, 133, 18038–18041

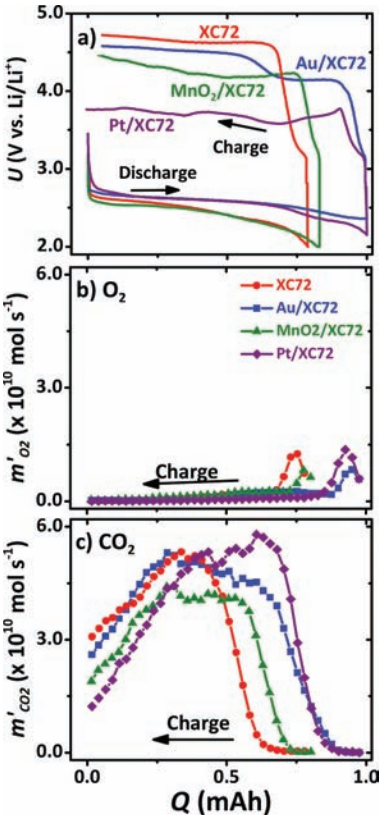

Figure 1. Gas evolution from cells employing 1PC:1DME. (a) Discharge−charge voltage curves, and corresponding O_2 (b) and CO_2 (c) evolution during charging of cells using various cathode catalysts. m'_i is the molar generation of species "i", U is cell output voltage, and Q is cell charge.

This voltage plateau remains unaffected regardless of whether a catalyst is used or not. A previous study indicated that the most likely source of this small O_2 evolution in PC-DME is Li_2O_2 decomposition (i.e., a small amount of Li_2O_2 is in fact formed during discharge in these solvents).[8] These facts raise an important question: what effect do these catalysts have when O_2 consumption and evolution is the dominant electrochemistry occurring in the cell?

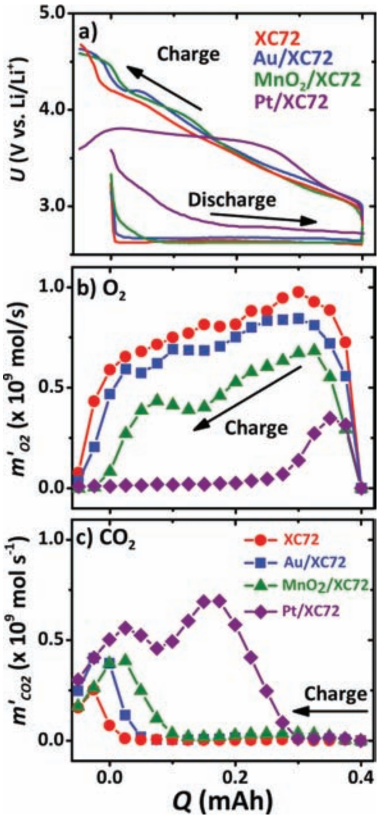

Figure 2. Gas evolution from cells employing DME. (a) Discharge−charge voltage curves, and corresponding O_2 (b) and CO_2 (c) evolution during charging of cells using various cathode catalysts.

Table 1. O_2 Consumed during Discharge and O_2 Evolved during Charge for Cells Studied in Figure 2

Cell cathode	O_2 consumed[a]	O_2 evolved[a]	OER/ORR
XC72	7.2	5.6	0.78
Au/XC72	7.2	5.0	0.69
MnO_2/XC72	5.5	3.3	0.60
Pt/XC72	5.3[b]	0.7	0.13

[a] In μmol of O_2 [b] Does not include 4.1 μmol of O_2 consumed at OCV.

To answer this question, we employed pure DME as the electrolyte solvent, as previous studies found that, in this solvent, Li_2O_2 was the dominant discharge product and O_2 evolution is the dominant charging process.[8] Figure 2 shows the first constant current discharge−charge cycle for DME-based cells using various cathode catalysts. The XC72, Au/XC72 (which was originally studied as an oxygen reduction reaction, and not an OER, catalyst[10]), and MnO_2/XC72 cells all exhibited similar discharge and charge voltages and similar voltage dependences for O_2 and CO_2 evolution. These facts imply that these nanoparticles do not act as oxygen evolution electrocatalysts when Li_2O_2 is produced during discharge. Although the Pt/XC72 cell had both a higher discharge and lower charge potential than the other cells, CO_2 is predominantly evolved during cell charge, indicating that Pt catalyzes DME decomposition in the presence of O_2. Pt was also found to catalyze the thermal decomposition of the electrolyte in the presence of O_2 at open circuit potential, as 4.1 μmol of O_2 was consumed at open circuit potential (OCV, Table 1). The OCV of the Pt/XC72 cell was much higher than the other cells (∼3.6 V) and most likely a result of this solvent decomposition chemistry. Pt is well-known to dissociate O_2 readily at room temperature,[11] so solvent decomposition likely is the result of the solvent reacting with adsorbed O-atoms on Pt.

Furthermore, O_2 evolution (Figure 2b) was largest and CO_2 evolution (Figure 2c) was smallest from the cell using a carbon-only cathode. For comparison, Table 1 presents the amount of oxygen reduced during discharge and the amount of oxygen evolved during charge for all cells studied in Figure 2. An XC72-based cell had a higher overall Coulombic efficiency (the ratio of oxygen evolution to oxygen reduction, OER/ORR) than any of the cells employing catalyst particles. The MnO_2/XC72 cell consumed and evolved less O_2 than the Au and carbon-based cells, presumably as a result of a portion of the discharge contributing to Li-ion intercalation into the α-MnO_2 structure. Nevertheless, the MnO_2/XC72 cell had a slightly lower Coulombic efficiency than the Au/XC72 cell.

In addition, using isotope labeling, we find that nearly all O_2 evolved during charging of all cells remained undissociated

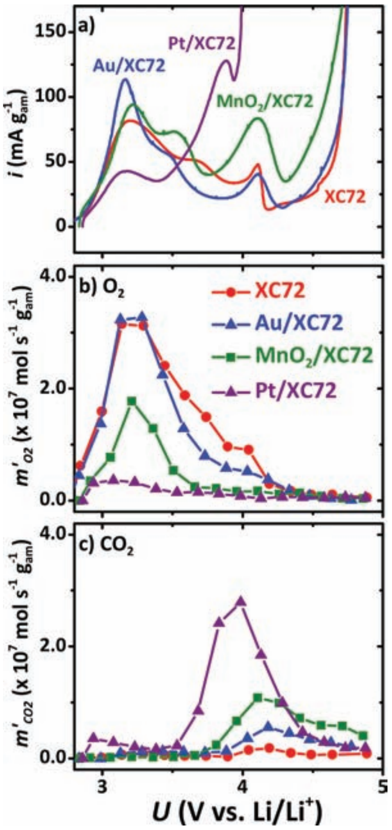

Figure 3. Gas evolution during oxidative potential scans. (a) Linear oxidative potential scans, and corresponding O_2 (b) and CO_2 (c) evolution during scans of DME-based cells using various cathode catalysts. "*i*" is mass-normalized cell current, "g_{am}" is the mass of the active material in the cell cathode (defined here as the sum of carbon and catalyst weight).

throughout the discharge−charge cycle,[12] indicating that O_2 had to be evolved from Li_2O_2 (O_2 evolution from decomposition of other Li compounds, such as LiOH or Li_2O, or from solvent decomposition would require O recombination and lead to isotope scrambling). During charge, the initial Coulombic efficiency (OER/ORR) is ∼1 in the XC72-based cell but decreases as the charging potential increases. This decreasing Coulombic efficiency is presumably due to some parasitic electrochemical reactions at higher operating potentials. Nevertheless, the potentials of all cells, regardless of the makeup of the cathode, are similar during the initial oxygen evolution/Li_2O_2 decomposition, which suggests no effective catalytic behavior compared to pure carbon.

Linear oxidative potential scans (Figure 3) were also performed on DME-based cells that were previously discharged with a small depth of discharge (33−50 mAh per gram of active material, where the active material included both the carbon and the catalyst particles). All gas evolution and currents were normalized to the weight of the cathode's active material. As seen in Figure 3a and b, the onset potential of O_2 evolution is nearly identical for each cell (∼2.9 V). Furthermore, the maximum current and O_2 evolution occur at nearly the same potential (3.2 V) for all cells. A second peak, in between 3.8 and 4.1 V, is present in all scans but corresponds primarily to CO_2 evolution, most likely from a PTFE binder contaminant that was reduced during discharge.

Figure 3 suggests that these nanoparticles do not act as electrocatalysts during Li_2O_2 oxidation. A true electrocatalyst lowers the kinetic barrier of the rate-determining charge transfer step and, hence, the kinetic overpotential (i.e., initial overpotential) for the overall electrochemical reaction. This reduction in the initial overpotential (relative to the carbon-only cathode) is not observed for any of the nanoparticles employed in Figure 3. In the context of aqueous ORR and OER, electrocatalysis reduces the overpotential by controlling the binding energy of the reaction intermediates to the electrocatalytic surface.[13] After the onset of charge transfer, other factors, e.g., transport limitations, affect the electrochemical rate at higher overpotentials and, hence, the shape of the full cyclic voltammetry curve. For example, the peak current in the potential scan typically occurs when the charge transfer rate and transport rates are equivalent. Recent calculations support the idea that, during oxidation, the major transport limitation is due to charge transport through the Li_2O_2 deposit from the C cathode.[14] We note that both Figures 2 and 3 show that full evolution of O_2 (complete oxidation of Li_2O_2) requires a significant increase in the charging potential above the O_2 onset potential.

A key question is why metal or metal oxide nanoparticles act as conventional electrocatalysts during charging of carbonate-based cells (where Li alkyl carbonate formation is the dominant discharge process), but not during charging of ether-based cells (where Li_2O_2 formation dominates)? To answer this question, consider the Li−O_2 electrochemical mechanism in a stable solvent, where a previous report suggests that discharge/charge involves sequential Li^+ induced charge transfer to surface adsorbed species ($O_2^* \rightarrow LiO_2^* \rightarrow Li_2O_2^*$ where * refers to a surface species).[15] In this case, the whole electrochemistry involves only ion transfers at the surface; i.e., there is no active solution species other than Li^+. While other mechanisms have also been proposed,[16,17] they all involve surface-adsorbed species (such as LiO_2) as the only intermediates. LiO_2 and Li_2O_2 are completely insoluble in nonaqueous electrolytes, as no ring current is observed in rotating ring disk experiments (RRDE) during Li−O_2 discharge using acetonitrile as a solvent (which produces Li_2O_2[17]).[18] True electrocatalysis requires that both the reactant and product of the rate-limiting step be mobile. Therefore, the reactant can diffuse to the catalytically active site and the product can diffuse away from it, allowing it to be used again. As was stated earlier, in carbonate-based solvents, effective CO_2 evolution electrocatalysis during charge is most likely a result of soluble mobile intermediate formation during the complex Li−O_2 electrochemistry. However, since there is no solution mobility of either LiO_2 or Li_2O_2 (as observed by the RRDE experiments discussed above), the only way electrocatalysis could proceed is if surface diffusion of both reactant and product (of the rate limiting step) is sufficiently fast over macroscopic distances to satisfy this criteria. Some surface diffusion of intermediates is expected, as crystalline Li_2O_2 growth is observed. However, this diffusion is apparently not fast enough for electrocatalysis to be effective. In addition, if any nanoparticles were catalytically active for discharge, the insoluble Li_2O_2 would rapidly coat the nanoparticles so that the catalytically active sites would be blocked during extended depths of discharge.

If nonaqueous Li−O_2 electrocatalysis is not effective, as our experiments indicate, we are led to the following question: is there a need for oxygen evolution electrocatalysts? As shown in Figure 3, for a low depth of discharge, oxygen evolution from each cell occurs at very low oxidative potentials, only slightly above the postdischarge open circuit voltage (∼2.8 V), which indicates that there is in fact only a very small overpotential for charging. Figure 2 shows that the same is true at the outset of charging for larger depths of discharge, and it is the initial O_2 evolution that is indicative of the kinetic overpotential for OER from crystalline Li_2O_2. The origin of the increasing oxidation potential evident in Figure 2 is currently under investigation. We speculate that this overpotential is more related to transport issues (and perhaps the stronger binding of some Li_2O_2 at defect sites) than to the fundamental kinetic overpotential. It is always possible, but not yet observed, that the inclusion of a nanoparticle may affect transport issues (such as the discharge electrodeposit conductivity) or binding energies in a favorable way to reduce the voltage range needed for full O_2 evolution during charging after deep discharges.

In conclusion, the formation of an insoluble and immobile species (Li_2O_2) on the cathode surface precludes transport of this species to active catalytic sites, making conventional OER electrocatalysis in Li−O_2 cells implausible. Efficient OER catalysis would lower the potential at which oxygen is first evolved. However, oxygen is initially evolved from low depth-of-discharge cells at a potential (~2.9 V) only slightly above the open circuit potential of the discharged cell (~2.8 V), which calls into question the need for conventional OER catalysts. Nevertheless, understanding the origin of the higher overpotentials that occur during full charging following deep discharges remains a key challenge. In part, this overpotential may be due to electron transport limitations through electrochemically grown Li_2O_2 films. Novel nanostructured cathodes or finding means to increase the electronic conductivity of the Li_2O_2 could help overcome this challenge and move us closer to achieving a high capacity rechargeable Li−air battery.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Materials and experimental methods (DEMS description, cathode preparation, electrochemical analysis). This information is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The authors gratefully acknowledge the entire IBM Almaden Reseach Center model shop for their efforts in creating many of the DEMS apparatus parts. We also thank Sally Swanson for synthesizing the α-MnO_2 nanowires.

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