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Molecular Level Understanding of Magnetism in Discharge Product and Oxygen Crossover Effect at the Anode in a Li-O_2 Battery using an Ether-based Solvent

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Abstract

Today's lithium-ion batteries do not provide sufficient energy for an acceptable driving distance, which has limited public interest in electric vehicles, particularly for long distance travel. Nonaqueous Li-air batteries have a much superior theoretical gravimetric energy density compared to conventional Li-ion batteries and thus have the potential for making long-range electric vehicles a reality. Reversible formation of lithium peroxide in these batteries, the properties of major/minor discharged products, stability of the non-aqueous electrolytes and oxygen crossover effect at the anode requires a molecular level understanding to achieve this reality. For the first time, we demonstrate that the major discharge product, lithium peroxide, formed in the lithium-air cell exhibits magnetic moment. These results are based on dc magnetization measurements and a Li-O_2 cell using an ether-based electrolyte. The results are unexpected since bulk Li_2O_2 is generally believed to be nonmagnetic with a significant band gap. Density functional calculations indicate a possible explanation as they find that "superoxide-like" O_2 surface groups with unpaired electrons exist on some *stoichiometric* lithium peroxide crystalline surfaces and on nanoparticle surfaces; these computational results are consistent with the magnetic measurement of discharged lithium peroxide product. The presence of "superoxide-like" O_2 surface groups with spin may play a role in the reversible formation and decomposition of the lithium peroxide as well as the reversible formation and decomposition of electrolyte molecules. We were also able to demonstrate that the crossover of O_2 from the cathode to the anode in Li-O_2 cells will result in different decomposition reactions occurring at the Li-anode than that in Li-ion batteries. The evidence indicates formation of LiOH as well as carbonates at the anode in a Li-O_2 battery with an ether-based electrolyte. In addition, the decomposition of the ether at the anode may result in fragments reaching the cathode and result in further deleterious reactions. Controlling reactions of ethers at the lithium anode through suitable membranes or passivation films will be essential for achieving good performance of Li-O_2 cells.