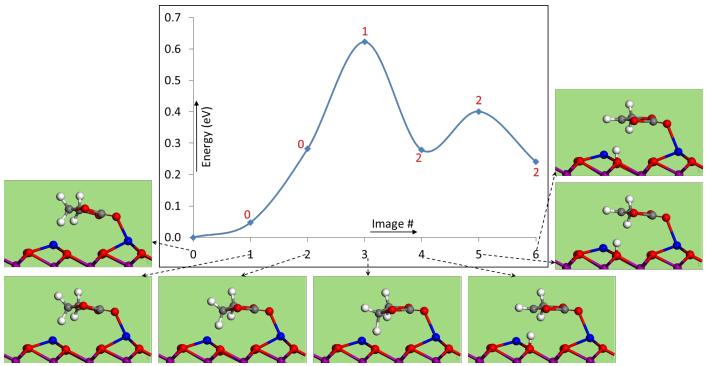
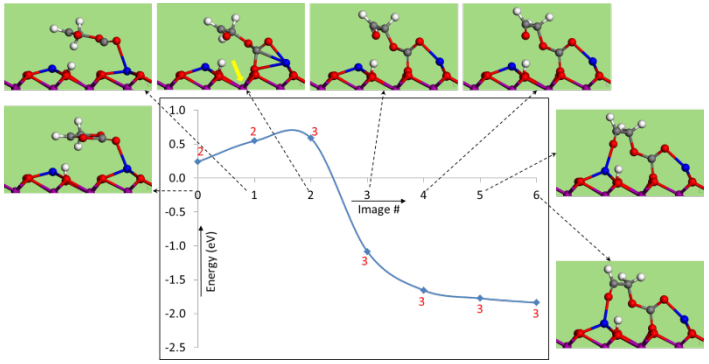
U.S.–China Clean Energy Research Center
中美清洁能源研究中心

Crystal Surface and State-of-Charge Dependencies of Electrolyte Decomposition on $LiMn_2O_4$ Cathodes



Top: The energy profile for H-abstraction, a possible reaction route for ethylene carbonate (EC) decomposition on the (111) surface of $Li_{0.67}Mn_2O_4$. The e- transferred from EC to slab (shown in red) ends up at bulk Mn ions.

Bottom: EC ring opening after H-abstraction. The yellow arrow shows the location of Mn ion that gained an e- which was transferred from EC.



Scientific Achievement

Predicted electrolyte decomposition reaction route with varying state of charge on the Li-ion cathode ($LiMn_2O_4$) (111) surface.

Significance and Impact

Identifies the preliminary reaction steps which could be precursor to the SEI-like thin film formation on this cathode surface.

Research Details

- Experimental studies have shown presence of stable, SEI-like thin film on the $LiMn_2O_4$ cathode (111) surface which contributes towards enhanced battery life by suppressing further electrolyte degradation and loss of active material (Mn dissolution) from the cathode. However, the mechanism underlying its formation is unclear.
- A rate determining proton transfer followed by ring opening of the EC is suggested as the reaction mechanism for the electrolyte degradation.
- The reaction rate of H-abstraction increases by a factor of 10^9, to a value of 10 reactions/sec when one-third of Li is removed from the cathode.

MICHIGAN

Work performed at Sandia National Laboratories and U. Michigan

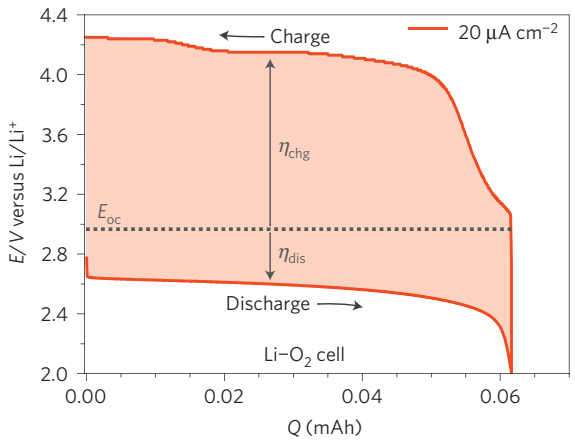
Kumar, Leung, and Siegel, *Crystal Surface and State of Charge Dependencies of Electrolyte Decomposition on $LiMn_2O_4$ Cathode, J. Electrochem. Soc. 2014, 161, E3059.* **DOI:** 10.1149/2.009408jes

U.S.–China Clean Energy Research Center
中美清洁能源研究中心

Na-air vs. Li-air

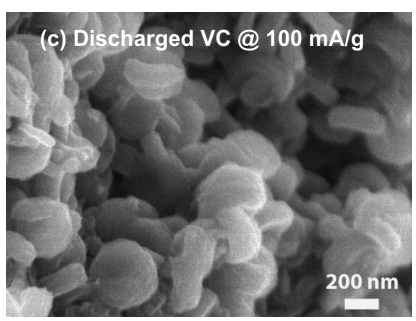
Na-O_2 batteries exhibit negligible overpotentials when discharged to NaO_2

Li-air: Li_2O_2 discharge phase

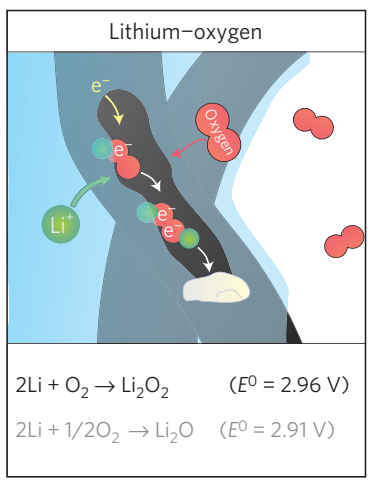


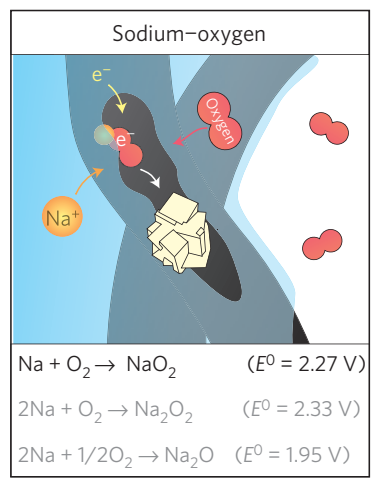
"…the large size of many product particles indicates at least a certain degree of electrical conductivity of NaO_2. As the electrical properties of NaO_2 have not been reported yet this has to be part of future investigations. For KO_2 a significant electric conductivity at room temperature is reported in the literature. [1]"

– *Nature Mater. 12, 228 (2013)* [1] J. Chem. Phys. 63, 2271–2278 (1975).

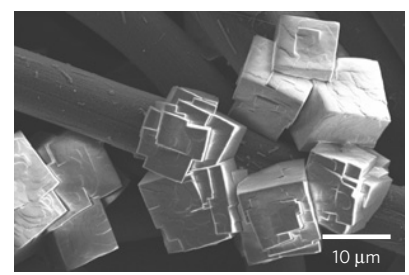


Energy Environ. Sci. 4, 2999 (2011)





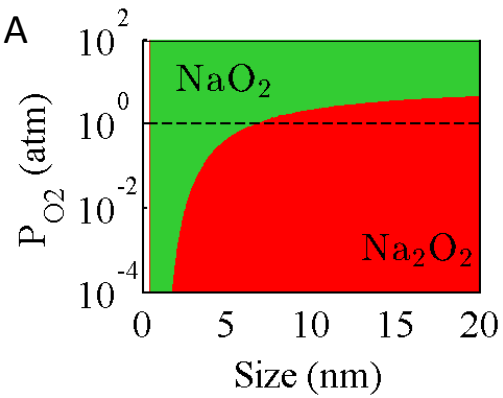
Nature Mater. **12**, 228 (2013)



U.S.–China Clean Energy Research Center
中美清洁能源研究中心

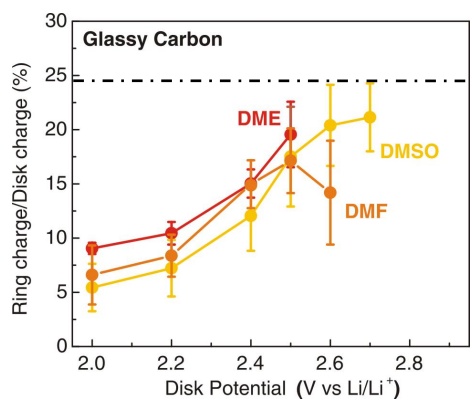
Growth Mechanisms and Chemistries of Discharge Products in Metal–O_2 Batteries

A



The phase diagrams of nanoscale NaO_2 and Na_2O_2 at 300 K as a function of O_2 partial pressure and particle size

B



Collection of soluble discharge reaction intermediates as a function of potential

Scientific Achievements

- The thermodynamic stability of bulk and particle phases of Na−O_2 compounds have been predicted as a function of temperature, O_2 partial pressure, and particle size using first principles calculations.
- The potential dependence of the lifetime of soluble intermediates involved in the Li-O_2 reaction was investigated for different candidate electrolyte solvents using the Rotating Ring Disk Electrode (RRDE) technique.

Significance and Impact

- Solved the puzzle in the formation conditions of discharge products and hinted at the direction to design higher performance Na−O_2 batteries.
- Showed that production of soluble species is higher at lower overpotentials, pointing to different growth mechanisms and hence morphologies of Li_2O_2 at different current densities.

Research Details

– The performance of Na−O_2 batteries is significantly influenced by the type of discharge product, either NaO_2 or Na_2O_2.

– While Na_2O_2 is a stable phase in bulk at the standard state, in nanoscale, lower surface energy stabilizes NaO_2 over Na_2O_2

S. Kang et al. Nano Letters 14 (2014)
doi:10.1021/nl404557w

Work was performed at MIT
Massachusetts Institute of Technology