



Energy Focus

Rechargeable room-temperature sodium-air battery involves sodium superoxide

With the growing presence of electric vehicles, there is an increasing drive to produce low-weight, high-capacity batteries that operate at room temperature. Significant attention has focused on lithium-air batteries, which reduce weight and volume by using atmospheric oxygen in place of an onboard reactant, and can thus rival the energy density of gasoline. Current lithium-air systems however suffer from several limitations, including complex chemistries and irreversible electrolyte decomposition during cycling. Addressing this problem, P. Hartmann of Justus Liebig University Giessen, Germany, A.K. Dürr of BASF, and their colleagues have demonstrated a reversibly charging/discharging sodium-air battery that may provide an alternative path to a rechargeable metal-air battery. Their results are reported in a letter published online December 2, 2012 in *Nature Ma-*

terials (DOI: 10.1038/NMAT3486).

A central issue for the performance of metal-air batteries is their ability to reversibly form and decompose a discharge product on the cathode. Lithium-air batteries reversibly form lithium peroxide (Li_2O_2) as a discharge product, although this currently requires non-trivial cathode materials (nanoporous gold) and a dimethyl sulfoxide-based electrolyte. Sodium-air batteries offer an alternative metal-air system, where previous work has focused on devices that formed sodium peroxide (Na_2O_2) as the discharge product. In common with the Li-based systems, these also suffered from large overpotentials and electrolyte decomposition.

To overcome these problems, Hartmann and his team developed a sodium-air system based on a sodium metal anode, glass microfiber separators, and a binder-free, carbon-fiber gas diffusion layer (GDL) cathode. The electrolyte was a 0.5 M solution of sodium triflate salt (NaSO_3CF_3) in anhydrous diethylene glycol dimethyl ether (DEGDME). No catalyst was used in the device, and the

cathode surface area was relatively low compared to analogous lithium-air batteries ($<1 \text{ m}^2/\text{g}$ versus $\sim 100 \text{ m}^2/\text{g}$).

The researchers were able to charge/discharge this system several times, with relatively low overpotentials ($<200 \text{ mV}$) and relatively high current densities ($0.5 \text{ mA}/\text{cm}^2$). Of particular note, the researchers found that the discharge product was highly pure crystalline sodium superoxide (NaO_2), which is not thermodynamically favored relative to Na_2O_2 . They hypothesize that this is due to the fact that NaO_2 requires the transfer of only one electron per formula unit (rather than two for Na_2O_2), making it kinetically favored.

The good performance of this battery suggests that sodium-air systems could display very attractive capabilities when optimized using techniques already explored in lithium-air systems. Combined with the simplicity of the cell reaction and the low cost of sodium, a sodium-based approach may therefore enable practical metal-air batteries to be realized.

Colin McCormick

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20-fs resolution pump-probe spectroscopy reveals role of hot exciton dissociation in polymer solar cells

Polymer solar cells consist of a blend of a semiconducting polymer donor with a fullerene derivative electron acceptor. The photoinduced dynamics at the interface between the donor and acceptor components are fundamental to light-to-current conversion. The precise mechanisms occurring on ultrafast time scales ($<100 \text{ fs}$), which involve excitons, interfacial states, and free charge carriers, remain to be explained. Using ultrafast absorption spectroscopy with very high, sub-20 fs time resolution, G. Grancini, G. Cerullo, G. Lanzani, and their colleagues from the Istituto Italiano di Tecnologia, the Politecnico di Milano, and Konarka Technologies (now Belectric) have now explored the impact of

the excitation energy on the formation of excited states in polymer solar cells.

The researchers used ultrafast transient absorption spectroscopy to reveal early time formation mechanisms of free charge carriers in poly[2,6-(4,4-*bis*-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b'] dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and [6,6]-phenyl- C_{60} -butyric acid methyl ester (PCBM) heterojunctions, as described in the December 9, 2012 online issue of *Nature Materials* (DOI: 10.1038/nmat3502). First, the researchers elucidate explicitly the time scale for exciton dissociation into interfacial states and free carriers: this process occurs in 50 fs for bandgap excitation. When the heterojunction is excited by photons with energies above the bandgap, hot excitons dissociate even faster into hot interfacial states, which in turn participate in the formation of free polarons. These fast processes compete effectively with other

relaxation pathways.

Density functional theory calculations for dimers of PCBM and a cyclopentadithiophene-benzothiazole (CPDTBT) oligomer also show that high-energy excitons and interfacial states are well coupled, and that the charge-transfer states are more delocalized when they are more energetic. Hence, rapid transition through hot states avoid the lowest lying, bound interfacial state and favor charge dissociation. Hot exciton dissociation through hot charge-transfer states also explains the internal quantum efficiency rise for high-energy excitations.

These findings are expected to encourage research in exploiting the energy collection from hot excitons and hot interfacial state manifolds in organic low-bandgap materials.

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