

Energy Focus
Champion nanostructures identified for solar water-splitting

Researchers from École Polytechnique Fédérale de Lausanne (EPFL) and the Technion-Israel Institute of Technology (Technion) have identified “champion” nanostructures able to produce hydrogen in the most environmentally friendly and cheap manner, by simply using daylight.

In the quest for the production of renewable and clean energy, photoelectrochemical cells (PECs) constitute a sort of Holy Grail. PECs are devices able to split water molecules into hydrogen and oxygen in a single operation, under

solar irradiation. “As a matter of fact, we’ve already discovered this precious chalice,” said Michael Grätzel, director of the Laboratory of Photonics and Interfaces (LPI) at EPFL. “Today we have just reached an important milestone on the path that will lead us forward to profitable industrial applications.”

As reported in the July 7 online edition of *Nature Materials* (DOI: DOI: 10.1038/NMAT3684), EPFL researchers, working with Avner Rothschild from the Technion, have accurately characterized the iron oxide nanostructures to be used in order to produce hydrogen at the lowest possible cost. “The whole point of our approach is to use an exceptionally abundant, stable, and cheap material: rust,” said Scott C. Warren, first author of the article who is now an assistant professor at the University of North Carolina at Chapel Hill.

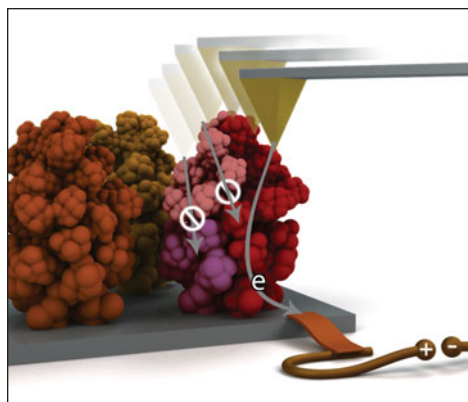
By analogy with those solar cells that achieve record performance—so-called “champion” solar cells—the researchers have developed a process for identifying champion nanostructures within water-splitting electrodes. By characterizing the structure of the aggregates of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) particles, and correlating this with their charge-transport characteristics, Grätzel’s research team was able to precisely characterize the movement of the electrons through the nanostructures, which were laid on electrodes during the manufacturing process. “These measures have helped us understand the reason why we get

performance differences depending on the electrodes manufacturing process,” said Grätzel.

Using dark-field transmission electron microscopy in combination with conducting atomic force microscopy, the researchers assessed the type of grain boundary which has the greatest influence on charge-carrier transport. “The majority carrier transport is limited primarily by high-angle grain boundaries rather than low-angle grain boundaries and imply that potential barriers form at many or most of the high-angle grain boundaries,” they reported.

By comparing several electrodes, whose manufacturing method is now mastered, scientists were able to identify the “champion” structure. By replicating that nanostructure across an entire electrode, the researchers succeeded in producing electrodes that split water with a record photocurrent. A 10×10 cm prototype has been produced and its effectiveness is in line with expectations. The next step will be the development of the industrial process to large-scale manufacturing.

Evidently, the long-term goal is to produce hydrogen—the fuel of the future—in an environmentally friendly and especially competitive way. For Grätzel, “current methods, in which a conventional photovoltaic cell is coupled to an electrolyzer for producing hydrogen, cost €15 per kilo at their cheapest. We’re aiming at a €5 charge per kilo.”



Conducting atomic force microscopy examines the charge-transport properties of individual $\alpha\text{-Fe}_2\text{O}_3$ (hematite) nanostructures, identifying champion nanostructures that produce solar hydrogen.

Energy Focus
Bifunctional poly(vinylpyrrolidone) binders enhance lithium sulfide cathode performance

Intercalation cathodes used in current lithium-ion batteries have a theoretical capacity of approximately 300 mA h g^{-1} . While this is sufficient for most commercial handheld electronics, it limits the widespread use of lithium-ion batteries in large-scale applications such as zero-emission electric vehicles. Although alternative next-generation

cathode materials such as sulfur and fully lithiated sulfur (Li_2S) demonstrate impressive theoretical capacities of 1673 mA h g^{-1} and 1166 mA h g^{-1} , respectively, the structural stability and long-term cycling performance of these electrodes are still unexplored.

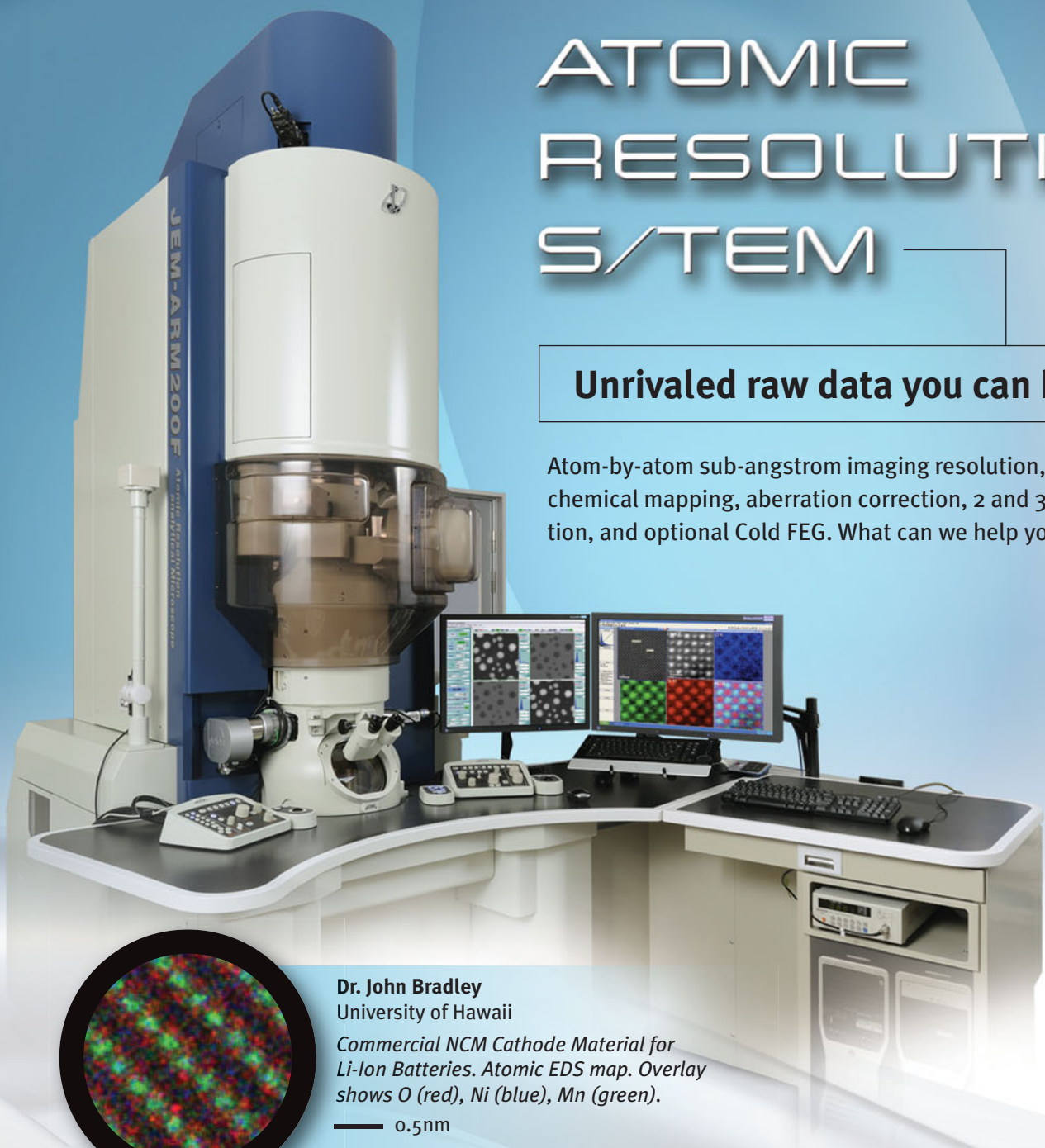
In the September issue of *Chemical Science* (DOI: 10.1039/c3sc51476e; p. 3673), a group of researchers from Stanford University, California, and Beihang University, Beijing, report improved structural stability and cycling of Li_2S cathodes through the use

of a bifunctional binder. Since previous studies have shown that compatible binders can significantly impair the overall performance of the electrode, Yi Cui’s group at Stanford and their collaborators focused on finding a new binder. This would replace the commonly used poly(vinylidene fluoride) (PVDF) for sulfur cathodes that displays strong affinity to Li_2S and lithium polysulfides (Li_2S_n , $4 \leq n \leq 8$). By using *ab initio* simulations to screen various functional groups often found in macromolecular binders and their bind-

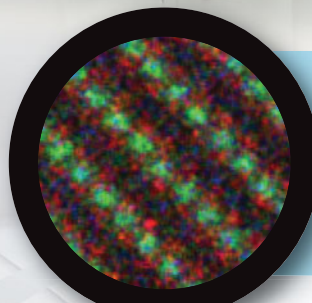
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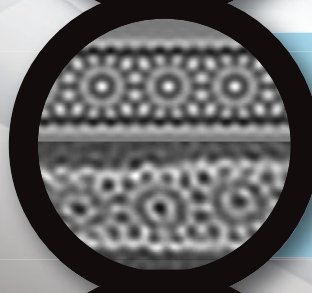
JEM-ARM200F



Dr. John Bradley
University of Hawaii

*Commercial NCM Cathode Material for
Li-Ion Batteries. Atomic EDS map. Overlay
shows O (red), Ni (blue), Mn (green).*

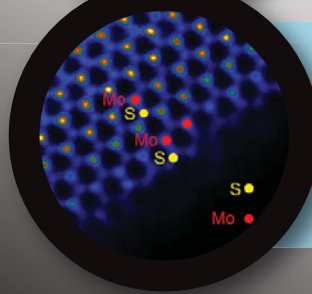
— 0.5nm



Dr. Miguel Jose Yacaman
University of Texas, San Antonio

Sample provided by Tour Lab, Rice University
*Chiral Nanotube with parameters $n=10$ and
 $m=4$ (simulated and experimental).*

— 0.5nm



Dr. Moon Kim
University of Texas, Dallas

*STEM HAADF image of transferred MoS_2 ,
showing Mo and S atom positions and their
 $2H$ stacking sequence.*

— 0.5nm

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ing energies with Li_2S , the researchers selected poly(vinylpyrrolidone) (PVP) as a promising choice due to the high affinity between the $>\text{C}=\text{O}$ groups in PVP and Li_2S and Li-S^\cdot species. Subsequent electrochemical testing with coin cells assembled with Li_2S cathodes using PVP binders confirmed their hypothesis.

The high binding energies of PVP with Li_2S and Li_2S_n allowed for uniform dispersion of the active material and carbon within the electrode and minimized loss of polysulfides into the electrolytes during cycling. These batteries also exhibited an initial specific capacity of 760 mA h g^{-1} and 94% capacity retention in the first 100

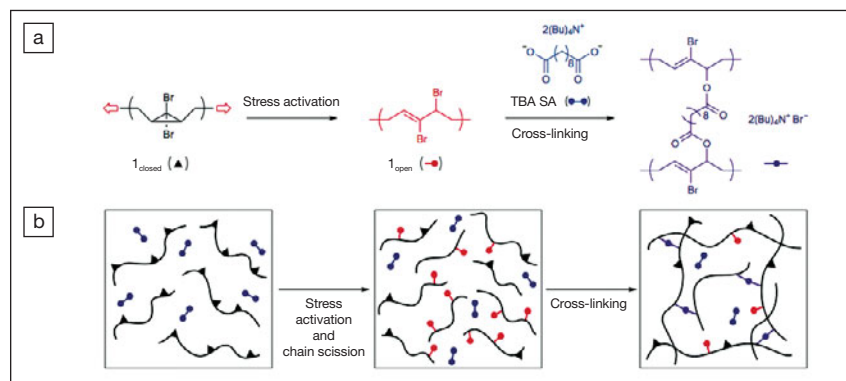
cycles. Even after 500 cycles, the PVP cells retained up to 69% of their initial capacity. The researchers envisage that their simple strategy of rational binder selection could be extended to the identification of new binders for other promising high-capacity electrode materials.

Dominica H.C. Wong

Shear forces self-strengthen mechanochemically active polymers

When polymeric materials are subjected to shear stresses, they typically suffer from bond breaking, which reduces their molecular weight and viscosity. Indeed, this is a problem that plagues oils and lubricants in high-performance engines. Now A.L. Black Ramirez of Duke University, J.A. Orlicki of the Army Research Laboratory, M. Champhekar of North Carolina State University, and their colleagues have developed synthetic polymers where the same forces responsible for the destructive processes of bond scission and chain disentanglement are channeled into constructive, bond-forming reactions.

As reported in the September issue of *Nature Chemistry* (DOI: 10.1038/nchem.1720; p. 757), the researchers inserted “mechanophores” (i.e., functional groups that respond to mechanical perturbation in a controlled manner) in the covalent backbone of the polymers, which enable remodeling and self-repair under mechanical stress. This concept of “activated remodeling through mechanochemistry” (ARM) is illustrated in the figure. Gem-dibromocyclopropanes (gDBCs, 1_{closed}) were embedded within a poly(butadiene) (PB) backbone as mechanophores, which provide the basis for self-repair through covalent cross-linking. When mechanically triggered, these undergo a ring opening polymerization, which leads to a 2,3-dibromoalkene product (1_{open}) open to nucleophilic substitution. The parent gDBC mechanophore is inert toward nucleophilic substitutions, so the repair reaction only occurs when sufficient forces are



Mechanochemistry self-strengthening concept: (a) A gDBC mechanophore within a polymer chain under tension undergoes a ring-opening reaction from 1_{closed} to 1_{open} . This increases the contour length and provides an allylic bromide that is capable of self-strengthening through nucleophilic displacement reactions. (b) System-wide force causes chain scission, but also activates the mechanophore (black triangle to red dot), which subsequently reacts with a cross-linker (blue) to form an active cross-link (purple) that overcomes the damage. Reproduced with permission from *Nature Chem.* 5 (2013), DOI: 10.1038/nchem.1720. © 2013 Macmillan Publishers Ltd.

experienced within the polymer to cause the non-scissile, ring-opening reactions.

The researchers tested the ARM response to shear forces of twin-screw extrusion, a common technique for processing bulk polymers. The conditions employed were destructive on a molecular level, where extrusion of 1_{closed} for 30 minutes at 40°C and 50 revolutions per minute generated bulk shear stresses of $0.15\text{--}0.25 \text{ MPa}$. While these caused bond scission and a reduction in molecular weight from 780 kDa to 560 kDa, these shear forces also mechanically activated the conversion of 7% of the gDBCs into their open form. In contrast, when the extrusion is repeated in the presence of suitable dicarboxylic acid molecules, which can cross-link the polymer chains via nucleophilic reaction with 1_{open} , the mechanically triggered cross-linking outcompetes the destructive shear forces during the extrusion process. The result is that the polymer becomes significantly stronger,

with an increase in the elastic modulus of nearly two orders of magnitude.

In the current system, remodeling takes place throughout the material and occurs in conjunction with irreversible deformation. However, the results raise the intriguing possibility of localized mechanochemical self-strengthening of “at-risk” regions within a load-bearing material. This research therefore has implications in various solid-state applications, where stress-induced bond scission or chain slippage triggers formation of microcracks, which propagate and eventually lead to material failure. Underlying the response is a new principle for materials design, in which chemomechanical coupling is used to capture otherwise destructive mechanical energy and funnel it into constructive processes. As in biological systems, it may be possible to actively remodel a synthetic material in response to its physical environment.

Jean Njoroge