with energy consumption of approximately 25 kWh per cubic metre of treated water<sup>4</sup>.

Joule heating of membrane surfaces via the application of electric current should be compared with other approaches, such as photothermal surface heating. One such approach involves the incorporation of plasmonic nanoparticles in the membrane structure, which are excited by electromagnetic irradiation to generate local heating<sup>11</sup>. This approach has recently been applied to enhance desalination performance of MD by incorporating silver nanoparticles in a thermal desalination membrane and irradiation by UV light to provide local surface heating of the membrane<sup>12</sup>. Employing photothermal desalination membranes with nanostructures that can generate effective local heating by

illumination with solar light can further improve the cost and energy efficiency of desalination by MD<sup>13</sup>. However, one of the major limitations of the photothermal approach for self-heating membranes compared with Joule heating via the application of electric current is the difficulty to irradiate a very large membrane surface area by UV or solar energy, which may limit this approach to small-scale MD systems.

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#### References

- . Shaffer, D. L. et al. Environ. Sci. Technol. 47, 9569–9538 (2013).
- Vidic, R. D., Brantley, S. L., Vandenbossche, J. M., Yoxtheimer, D. & Abad J. D. Science 340, 1235009 (2013).
- Gregory, K. B., Vidic, R. D. & Dzombak D. A. *Elements* 7, 181–186 (2011).
- Tong, T. Z. & Elimelech, M. Environ. Sci. Technol. 50, 6846–6855 (2016).
- Lin, S., Yip, N. Y. & Elimelech, M. J. Membrane Sci. 453, 498–515 (2014).
- Dudchenko, A. V., Chen, C., Cardenas, A., Rolf, J. & Jassby, D. Nat. Nanotech. 12, 557–563 (2017).
- Gupta, R., Rao, K. D. M., Kiruthika, S. & Kulkarni, G. U. ACS Appl. Mater. Interf. 8, 12559–12575 (2016).
- Liu, P., Liu, L. A., Jiang, K. L. & Fan, S. S. Small 7, 732–736 (2011).
- 9. Mistry, K. H. et al. Entropy Switz. 13, 1829–1864 (2011).
- Thiel, G. P., Tow, E. W., Banchik, L. D., Chung, H. W. & Lienhard, J. H. Desalination 366, 94–112 (2015).
- 11. Politano, A. et al. J. Phys. Condens. Mat. 28, 363003 (2016).
- 12. Politano, A. et al. Adv. Mater. 29, 1603504 (2017). 13. Westerhoff, P., Alvarez, P., Li, Q. L., Gardea-Torresdey, J.
- Westernon, P., Alvarez, P., Li, Q. L., Gardea-Torresdey, J.
  & Zimmerman, J. Environ. Sci. Nano 3, 1241–1253 (2016).

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## LITHIUM-OXYGEN BATTERIES

# The reaction mechanism revealed

Using *insitu* environmental transmission electron microscopy, the structural and phase changes of the reaction products of an air cathode during discharging and charging can be visualized in real time.

#### Yang-Kook Sun and Chong S. Yoon

ith increasing deployment of electric vehicles and largeformat energy storage systems, Li battery technology is on the verge of transforming the way we use and distribute energy worldwide. However, conventional lithium-ion batteries1 cannot satisfy the energy density requirements of mid- and large-scale systems. Due to their theoretical specific energy density, which is about 10 times higher than that of lithium-ion cells, lithium-oxygen  $(Li-O_2)$  batteries are in the spotlight as a potentially viable way forward<sup>2,3</sup>. Despite these promises, however, the reaction mechanism during charging and discharging of Li-O<sub>2</sub> batteries is still unclear. Writing in Nature Nanotechnology, Luo et al. now report an in situ transmission electron microscopy (TEM) analysis that provides important insights on the physico-chemical reaction pathway between O<sub>2</sub> and the Limetal anode during oxygen reduction and oxygen evolution reactions<sup>4</sup>.

Various analytical methods have been applied to capture the formation and decomposition of reaction products in Li–O<sub>2</sub> batteries. The formation of Li<sub>2</sub>O<sub>2</sub> toroidal structures nucleating on a carbon fibre surface during discharge<sup>5</sup>, as well



**Figure1** Reaction products of a Li– $O_2$  cell. **a**, Schematic illustration of formation and collapse of the reaction products in the Li– $O_2$  battery during discharging (oxygen reduction reaction, ORR) and charging (oxygen evolution reaction, OER) observed by *insitu* environmental TEM. **b**, *Ex situ* TEM image of the reaction product in the Li– $O_2$  battery illustrating the chemistry of the discharge product. The red arrow indicates the escape of  $O_2$  from the hollow particle. The main reaction product is labelled in yellow and the surface passivation layer is indicated by the green dashed line. The inset shows the hollowness of the spherical particles. Panel **b** adapted from ref. 7, American Chemical Society.

as hollow Li<sub>2</sub>O<sub>2</sub> structures, have been observed<sup>6.7</sup>. To understand the decomposition of Li<sub>2</sub>O<sub>2</sub> during charging, *in situ* TEM experiments were carried out in vacuum, but in this way only the decomposition of preformed  $\text{Li}_2\text{O}_2$  structures could be observed<sup>8</sup>. The main experimental advance of Luo *et al.* is to have carried out their investigation under  $O_2$  atmosphere using an environmental TEM. The  $O_2$  gas is kept at a constant pressure, simulating the same oxygen-rich environment of a real Li– $O_2$ battery during operation. This setup enabled the researchers to directly observe a full electrochemical cycle, clarifying the chemistry as well as the growth and decomposition kinetics of the reaction products.

Luo et al. use Li<sub>2</sub>O formed on the surface of Li metal as a solid electrolyte, and carbon nanotubes dressed with a RuO<sub>2</sub> nanoparticle catalyst as a cathode (the catalyst enables the reversible formation and decomposition of reaction products). Upon discharging, the researchers observe the formation of hollow spheres at the contacting sites between the nanotubes, Li<sup>+</sup>, and O<sub>2</sub>. These spheres grew up to ~50-200 nm in size during the oxygen reduction reaction; and shrank and collapsed to crumpled shells within a few minutes during the oxygen evolution reaction (Fig. 1a). Luo et al. also observe other unique morphologies after partial charge - these are the result of a local inward contraction of the shell<sup>4</sup>. As a general validation of this mechanism, ex situ TEM images show hollow, crumpled, and ruptured spherical structures that are remarkably similar to the ones observed in situ.

The formation mechanism of such structures has remained unexplained

due to an inability to investigate the intermediate chemical species, and this work provides clear insights on this aspect. In an oxygen-rich environment and in the presence of a solid electrolyte, LiO<sub>2</sub> structures covered by Li<sub>2</sub>O are the initial discharging products. LiO<sub>2</sub> is subsequently converted to  $Li_2O_2$  and  $O_2$ through a disproportionation reaction inside the particle (Fig. 1b). The released  $O_2$  gets trapped inside the nanostructures, inflating them and finally forming hollow structures. Meanwhile, a Li<sub>2</sub>O passivation film forms on their surface by  $O_2 + 4Li^+ + 4e^- \rightarrow Li_2O$  so that at the end of the discharge the final products are Li<sub>2</sub>O and Li<sub>2</sub>O<sub>2</sub>. The Li<sub>2</sub>O outer layer protects the particle from cracking and this is why these structures remain stable even in ex situ experiments.

The direct observation of the metastable nature of  $\text{LiO}_2$  during oxygen reduction and oxygen evolution reactions confirms the conclusions of a previous work in which crystalline  $\text{LiO}_2$  was detected indirectly by stabilizing the intermediate phase using iridium nanoparticles<sup>9</sup>.

In their *in situ* TEM experiments, Luo *et al.* employ a solid electrolyte out of necessity — the reaction mechanism of which can differ from that of an organic liquid electrolyte used in practical Li– $O_2$  cells. However, Luo and colleagues' interpretation of the formation and decomposition of discharge products agrees well with other *ex situ* TEM results obtained using a liquid electrolyte<sup>6,7</sup>.

There remains much work to be done to make  $\text{Li}-O_2$  batteries practical, especially on the materials and the cell-design side. But the observation and nanoscale physico-chemical elucidation of the cell operation mechanism is a solid foundation for future  $\text{Li}-O_2$  battery designs and optimization.

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#### References

- 1. Lee, J. et al. Energy Environ. Sci. 9, 2152-2158 (2016).
- 2. Bruce, P. G. et al. Nat. Mater. 11, 19–29 (2012).
- 3. Lu, J. et al. Chem. Rev. 114, 5611–5640 (2014).
- 4. Luo, L. et al. Nat. Nanotech. 12, 535–539 (2017).
- Mitchell, R. R., Gallan, B. M., Thompson C. V. & Shao-Horn, Y. Energy Environ. Sci. 4, 2952–2958 (2011).
- Jung, H.-G., Hassoun, J., Park, J.-B., Sun, Y.-K. & Scrosati, B. Nat. Chem. 4, 579–585 (2012).
- 7. Jung, H.-G. et al. Nano Lett. 12, 4333-4335 (2012).
- 8. Zhong, L. et al. Nano Lett. 13, 2209-2214 (2013).
- 9. Lu, J. et al. Nature 529, 377-382 (2016).

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# A light-powered clockwork

An organogel is made of molecular motors and modulators that act cooperatively to perform a full mechanical cycle of contraction and expansion at the macroscale.

## Chenfeng Ke

he field of molecular machines, first envisioned by Richard Feynman in 1961<sup>1</sup>, was recognized with the 2016 chemistry Nobel prize<sup>2</sup>. The synthetic machines of Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa can be operated upon by external stimuli such as light<sup>3</sup>, pH change<sup>4</sup> or oxidation/reduction<sup>5</sup>, thereby undergoing translational motions or rotations. A challenging next step consists of amplifying these molecular-level mechanical movements to obtain a sizeable effect at the macroscale<sup>6</sup>. The random orientation of these molecular machines in solution, however, results in no useful work being performed at the macroscale. To overcome

this obstacle, nanomachines should be assembled in a controlled manner to achieve synchronized molecular motion. Writing in *Nature Nanotechnology*, Foy *et al.* now report an organogel that can reversibly contract and expand as a result of the photoactuation of two molecular machinery parts (a unidirectional motor and a switchable modulator) embedded in it<sup>7</sup>. The operation is similar to a mechanical watch in which the winding of the mainspring transfers energy to turn gears and run the hands on a dial (Fig. 1).

The first component of the system by Foy *et al.* is a Feringa-type light-driven unidirectional molecular motor<sup>3</sup>. This consists of a bis-helicene backbone connected by an alkene double bond with axial chirality and two stereocentres. The rotary cycle is made of four steps (Fig. 2a). First, a photoisomerization rotates the rotor clockwise to approach the stator, resulting in a high-energystate conformation. Subsequently, this high-energy rotor moves across the stator to reach a thermodynamically favourable conformation that prohibits the rotor from going back. A second photoisomerization followed by a helix-inversion completes the cycle. Continuous photoirradiation makes these motors rotate up to megahertz frequencies<sup>8</sup>.

In solution, an Avogadro's number of these motors would rotate unidirectionally