Inspiration from surfactants gives Li-S cells longer life

The renewable-fuelled future is reliant on improvements in battery energy density to smooth the grid and power electric vehicles for longer journeys. Lithium-ion cells – the industry standard – are almost at their capacity. Lithium-sulfur cells could be the answer, current technology degrades quickly due to an effect called redox shuttling. Dr Gao Liu, a staff scientist at the Lawrence Berkeley National Laboratory, have taken inspiration from surfactants to redesign electrolytes. Hydrofluoroethers (HFE) additives encapsulate lithium ions in micelle-like structures, without problematic polysulfides dissolution.

LI-ION CELLS: UP TO THE JOB?
For a world run on renewables, new technology is required which can store energy from intermittent renewable sources. Since lithium-ion cells first hit the market in 2019, they have received enormous investment. Battery packs cost 11% of what they did a decade ago, and are used for industrial electricity storage for grid-balancing down to the mobile phones.

However, one obvious problem is the availability of these megawatt-hours. Solar panels can only output electricity when the sun is shining, and turbines only turn when the wind is blowing.

The other big barrier is the transportation of this power. Vehicles are a large energy consumer, and the source is almost always fossil fuels.

More than 70% of the world’s energy supply is from coal and gas. However, with the price of solar in decline – it dropped 89% between 2009 and 2019 – things are on the turn. Solar, only recently the most expensive megawatt-hours on the market, is now cheaper than gas, nuclear and coal.

However, renewable energy in the U.S. still stood at a rather measly 10% of all energy consumption in 2019. So what stands in the way of the renewable revolution?

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LI-S: THE REDOX SHUTTLE
One exciting emerging technology is lithium-sulfur (Li-S) cells, promising a higher theoretical energy density – around 2600 Wh/kg – using abundant and inexpensive materials.

A Li-S cell contains two electrodes: the anode composed of lithium metal and the cathode composed of sulfur. As it discharges, lithium dissolves in the electrolyte between the electrodes and travels to the cathode. At the cathode, sulfur molecules react with lithium ions Li⁺, forming Li₂S₄.

As more lithium travels to the cathode, further reactions occur, forming other lithium polysulfide molecules: Li₂S₄, Li₂S₆, eventually Li₂S. During charging, the opposite occurs.

Or at least, that’s the theory. Lithium polysulfide Li₂S₄ and Li₂S₆ are highly soluble in the electrolyte of the cell. As a result, they diffuse throughout the cell. When a lithium polysulfide molecule reaches the lithium anode, it reacts to form a shorter-chain polysulfide like Li₂S₂ and Li₂S₄, depositing some sulfur at the anode.

This molecule can travel between the anode and cathode, picking up atoms from the sulfur electrode and depositing them at the lithium electrode. Over several charge-discharge cycles, this ‘redox shuttling’ effect decreases the capacity of the cell.

FIXING THE REDOX SHUTTLE
Attempts to limit redox shuttling in Li-S cells have generally involved creating a barrier to prevent lithium polysulfide molecules from reaching the anode. However, creating these barriers – for example, by modifying the lithium electrode to only allow lithium ions through – is complicated and costly.

Dr Gao Liu is a staff scientist at the Lawrence Berkeley National Laboratory. He has worked recently took a different approach to limiting redox shuttling. Instead of modifying the electrodes, their work involves modifying the electrolyte which is sandwiched between the two electrodes.

This approach has some heritage in the research literature: other groups have found certain electrolytes which have a preference for dissolving lithium salts over lithium polysulfides. Once the lithium ions have ‘used up’ the solvation coordination sites, there is little room for the solvation of lithium polysulfide molecules.

However, the conclusion of much of this research is a resort to high-viscosity solvents which have a problem of their own: poor lithium transport, where slow lithium diffusion leads to poor cell performance.

INSPIRATION FROM SURFACTANTS
The Liu group have recently published a work detailing how they have taken inspiration from surfactants to create electrolytes with “localized high concentrations” of lithium salts. Their work involves using hydrofluoroethers (HFEs), a class of solvents that has previously been shown to preferentially dissolve lithium salts over lithium polysulfides. HFE molecules used up until now have generally contained a central oxygen atom, with fluorinated carbon chains on either side. The oxygen atom binds to lithium, whereas the fluorinated chains are chemically inert.

These fluorinated chains are the reason for the solvation preference of lithium ions over lithium polysulfides. The fluorinated chains block the approach of a bulky lithium polysulfide molecule to the oxygen atom. However, small lithium ions are able to approach the oxygen atom unhindered.

The Liu group’s most recent research takes this idea one step further, instead of having a single ether bond in a central position of the solvent molecule, they have taken inspiration from

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surfactants, to use HFEs with an ether section on one end and a fluorinated section on the other. These molecules are designed to mimic surfactant molecules, which have hydrophobic and hydrophilic sections, allowing the dissolution of oil molecules in water. In the same vein, the ether section of these specialised HFE molecules is considered “lithiophilic” (lithium-loving) and the fluorinated section “lithiophobic.” Liu refers to this as a “Janus” structure, in reference to the two-faced Roman god.

**CAN THESE FORM MICELLES?**

The researchers hypothesise that when this HFE is added to a fluorinated solvent, lithium salts are solvated in a special mechanism, involving the formation of nano-sized micelle-like structures. These structures are a shell of HFE molecules, lithiophilic ether sections facing inwards and the fluorinated section ‘lithiophobic’. Considered ‘lithiophilic’ (lithium-loving) structures are spontaneously formed, and the first report of a micelle-like structure being used in a lithium-cell electrolyte.

**A MEANS TO AN END**

Suppressing lithium polysulfide dissolution in Li-S electrolytes is a means to a very specific end: a viable lithium-sulfur cell. It's important to ensure that these micelle-like structures are electrochemically stable. Key signs of success are coulombic efficiency and cycling stability – in other words, is energy wasted during charging, and does the cell retain its capacity after repeated charge-discharge cycles? To test this, the group measured the cycling performance of various Li-S cell electrolyte/ additives in 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) with different additive/solvent ratios. These were compared to a benchmark electrolyte, DOL in DME.

Whilst a 1:1 ratio of HFE to TTE performed poorly on coulombic efficiency, a 1.5 ratio of HFE to TTE performed far better than the benchmark, HFE additives are chemically stable when used alongside the lithium electrode. These tests demonstrate that the group's electrolyte is more chemically stable than the benchmark electrolyte. Even after 200 charge-discharge cycles, the coulombic efficiency was about 99.5%, and was only slightly compromised at the highest current densities tested.

**EVIDENCE FOR SUPERIOR PERFORMANCE**

A final important factor in cell life is the effect of each charge cycle on the lithium anode. To test this, the group created test cells with one lithium electrode – as in the Li-S cells – but replacing the sulfur electrode with a copper one. These tests were designed to establish whether the dissolved lithium polysulfide...