

REDOX FLOW BATTERIES

Tanking up energy through atypical charging

Designed ketone molecules can undergo two-electron charge storage in aqueous solutions

By **Bo Hu** and **T. Leo Liu**

Aqueous redox flow batteries could provide viable grid-scale electrochemical energy storage for renewable energy because of their high-power performance, scalability, and safe operation (1, 2). Redox-active organic molecules serve as the energy storage materials (2, 3), but only very few organic molecules, such as viologen (4, 5) and anthraquinone molecules (6), have demonstrated promising energy storage performance (2). Efforts continue to develop other families of organic molecules for flow battery applications that would have dense charge capacities and be chemically robust. On page 836 of this issue, Feng *et al.* (7) report a class of ingeniously designed 9-fluorenone (FL) molecules as high-performance, potentially low-cost organic anode electrolytes (anolytes) in aqueous organic redox flow batteries (see the figure, top). These FL anolytes not only display exceptional energy storage performance but also exhibit an unprecedented two-electron storage mechanism.

The past decade has witnessed the rapid development of aqueous organic redox flow batteries using sustainable and tunable redox-active organic molecules as charge storage materials (2, 8, 9). Previous studies investigated the possibility of using organic ketones as anolyte materials but with limited success (10, 11), and Rodriguez *et al.* (11) reported the one-electron, reversible FL/FL^{•-} redox couple in alkaline solutions. However, the poor battery performance of FL molecules was not suitable for durable energy storage, and there was no clear understanding of FL's chemical stability (11).

Feng *et al.* report the molecular engineering of FL molecules to achieve substantially improved stability and charge capacity for flow battery applications. The strategy adopted in their research is to introduce electron-withdrawing groups (EWGs),

such as sulfonate and carboxylate groups, into the aromatic rings of FL to increase the acid dissociation constant K_a of its reduction product, FL-OH. This design aims to stabilize the charged FL species, such as FL^{•-} radical anions and FL²⁻ dianions, for battery cycling by avoiding the irreversible protonation of these anions and allowing the redox reactions to occur in the potential window available in water (see the figure, bottom). Their density functional theory calculations of a series of FL-OH derivatives also suggest that EWGs effectively increase the K_a of both O-H

and benzylic C-H protons. Upon functionalization of FL with EWGs, the first electron reversibility of FL at ~ -0.7 V versus the normal hydrogen electrode is notably improved in alkaline solutions. Nevertheless, the second electron redox event at ~ -1.13 V is still irreversible, as revealed in cyclic voltammetry studies, but is accessible for energy storage, as explained below.

For flow battery demonstration, the authors chose 2-carboxylate-7-sulfonate fluorenone (4C7SFL). A solution of 1.36 M 4C7SFL in NaOH was used as an anolyte with a mixture of $K_4Fe(CN)_6/K_3Fe(CN)_6$ as a cathode electrolyte (catholyte). At room temperature, the 4C7SFL/ferrocyanide flow batteries delivered a high energy efficiency of 78.8% at 60 mA cm⁻². The battery was cycled at 20 mA cm⁻² for more than 4 months and had a small capacity decay of 2.62%—equivalent to a capacity decay of 0.02% per day. The exceptional chemical stability of 4C7SFL was confirmed by postcycling spectroscopic studies that revealed only a small amount of a desulfonated product. Notably, the 4C7SFL anolyte actually exhibited two-electron storage capacity (equivalent to 1.8 moles of electrons per 1.0 mole of 4C7SFL) in the battery studies, despite the control of the charge and discharge processes at the FL/FL^{•-} redox couple.

At first glance, it would seem impossible that an irreversible redox process such as the second-electron reduction of 4C7SFL could be used for energy storage under these conditions. Feng *et al.* propose that the two-electron storage property of 4C7SFL originates from the disproportionation of a FL^{•-} radical anion, rather than the electrochemical reduction of FL^{•-} to FL²⁻. During the charging process, electrochemically generated FL^{•-} disproportionates to FL-OH, a two-electron reduced product, and FL. The regenerated FL undergoes reduction again until an equilibrium is reached under battery-charging conditions.

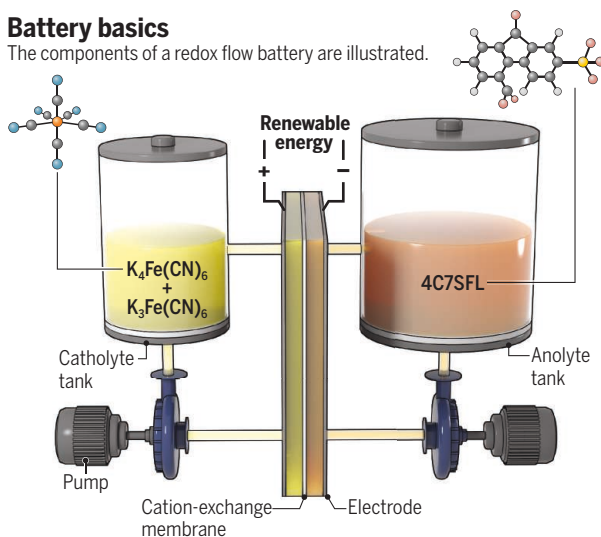
This hypothesis is supported by nuclear magnetic resonance spectroscopy studies that detected the

Extra electrons without catalysts

Feng *et al.* demonstrated an aqueous organic redox flow battery based on reversible hydrogenation of functionalized 9-fluorenone (2-carboxylate-7-sulfonate fluorenone, or 4C7SFL). This molecule enabled two-electron storage without the use of a catalyst.

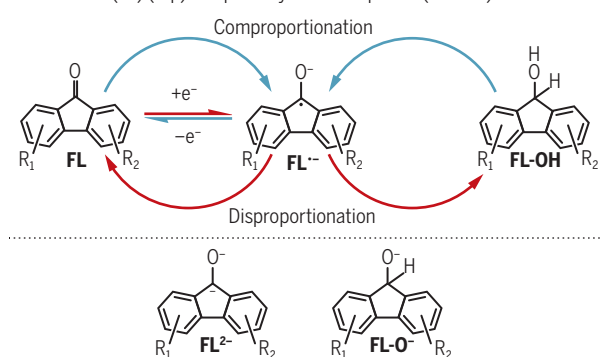
Battery basics

The components of a redox flow battery are illustrated.



Charging and discharging molecules

Charging (red arrows) and discharging (blue arrows) mechanism of 9-fluorenone (FL) (top) and possibly involved species (bottom) are shown.



FL-OH product, 4C7SFL-OH, even at a 25% state of charge. The authors also studied the comproportionation reaction by combining 4C7SFL and 4C7SFL-OH, and they detected a small amount of the $[4C7SFL]^-$ radical by electron paramagnetic resonance spectroscopy. The FL^- generated from the comproportionation can be used for electrochemical discharge. These studies suggest that an equilibrium exists between FL^- , FL, and FL-OH, and also favors the disproportionation.

The formation and cleavage of the benzylic C-H bond of FL in the disproportionation and comproportionation reactions are likely regulated by subtle proton-coupled electron transfer processes that are subject to further study. The singly protonated species, $FL-O^-$, may be the final charged state and involves the chemical reactions under the strong alkaline condition. In addition, the reduction of ketones to alcohols typically involves a catalyst (12), so the reversible, uncatalyzed hydrogenation of FL represents an unusual two-electron storage mechanism for flow battery applications and is mechanistically different from the direct electrochemical two-electron reduction of viologen and anthraquinone anolytes (2).

The work by Feng *et al.* expands the selection of stable organic anolytes and serves as a good example of rational molecular engineering to develop durable electrolyte materials. However, a large excess of the $K_4Fe(CN)_6/K_3Fe(CN)_6$ catholyte was needed in the flow battery tests because of the long-term instability of ferro- and ferricyanide in alkaline solutions (13). Thus, developing catholyte molecules with durabilities and capacities comparable to those of fluorenone, viologen, and anthraquinone anolyte molecules is urgently needed to fully unleash the energy storage potential of aqueous organic redox flow batteries. ■

REFERENCES AND NOTES

1. B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **334**, 928 (2011).
2. J. Luo, B. Hu, M. Hu, Y. Zhao, T. L. Liu, *ACS Energy Lett.* **4**, 2220 (2019).
3. M. Park, J. Ryu, W. Wang, J. Cho, *Nat. Rev. Mater.* **2**, 16080 (2016).
4. B. Hu, C. DeBruler, Z. Rhodes, T. L. Liu, *J. Am. Chem. Soc.* **139**, 1207 (2017).
5. J. Luo *et al.*, *Joule* **3**, 149 (2019).
6. Y. Ji *et al.*, *Adv. Energy Mater.* **9**, 1900039 (2019).
7. R. Feng *et al.*, *Science* **372**, 836 (2021).
8. J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager, U. S. Schubert, *Angew. Chem. Int. Ed.* **56**, 686 (2017).
9. Y. Ding, C. Zhang, L. Zhang, Y. Zhou, G. Yu, *Chem. Soc. Rev.* **47**, 69 (2018).
10. P. Leung *et al.*, *Appl. Energy* **197**, 318 (2017).
11. J. Rodriguez Jr., C. Niemet, L. D. Pozzo, *ECS Trans.* **89**, 49 (2019).
12. O. Eisenstein, R. H. Crabtree, *New J. Chem.* **37**, 21 (2013).
13. J. Luo *et al.*, *Nano Energy* **42**, 215 (2017).

ACKNOWLEDGMENTS

The authors acknowledge funding support from the National Science Foundation (Career Award, grant 1847674) and a Utah State University faculty start-up.

10.1126/science.abi5911

SYMBIOSIS

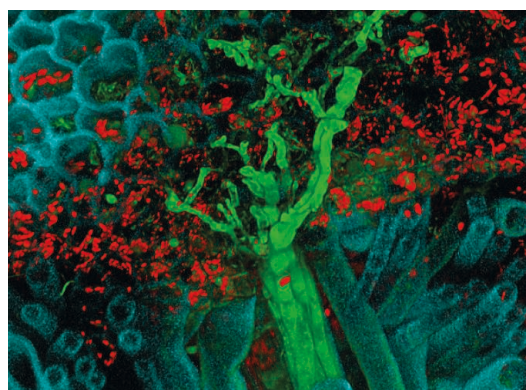
Plant lipids enticed fungi to mutualism

Evolution of lipid transfer from plants to fungi allowed plants to colonize land

By Harro J. Bouwmeester

The migration of plants from water to newly emerged land some 450 million years ago required plants to acquire a number of crucial new traits. Fossil records provide compelling evidence that one of these traits is the symbiosis (or mutualism) between these early land plants and arbuscular mycorrhizal (AM) fungi. On page 864 of this issue, Rich *et al.* (1) show that the primitive land plant *Marchantia paleacea* produces lipids that are transferred to the fungus and that this process is essential for a functional symbiosis (see the image). This localized lipid biosynthesis also occurs in higher plants that engage in symbiosis with AM fungi (2, 3), but not in algae, suggesting

can take up water, phosphorus, nitrogen, and other elements that the plant cannot reach (4). For a long time, it was assumed that plants, in return for the resources supplied by the fungus, provided carbohydrates from photosynthesis to the fungus. Only recently, it was discovered that in addition to carbohydrates, plants also supply lipids to the fungus (2, 3). To investigate how old this mechanism is, Rich *et al.* used an elegant approach: a comparison of RNA sequencing gene expression data on the AM fungal interaction in the primitive *M. paleacea* with data of AM fungal interactions in higher plants. With this comparison, the authors show that orthologs of many of the known higher-plant symbiotic genes are also expressed in *M. paleacea* upon AM fungal colonization, confirming conservation across 450 million years of plant diversification [also see (5)]. Rich *et al.* report that this includes genes that have been shown in higher plants to be responsible for lipid exchange from the plant to the fungus, such as the lipid biosynthesis-related *REQUIRED FOR ARBUSCULAR MYCORRHIZATION 2* (*RAM2*) and the lipid transporter *STUNTED ARBUSCULE 1* and *2* (*STR1* and *STR2*) (see the figure). With a number of experiments, they subsequently show that *M. paleacea* is indeed producing lipids and that they are essential for the symbiosis with AM fungi.



The confocal microscopy image shows a symbiotic fungus (*Rhizophagus irregularis*) colonizing the liverwort *Marchantia paleacea* (plant cell walls, cyan; chloroplasts, red; fungus, green).

that this process evolved 450 million years ago, allowing plants to colonize land, and is conserved across the plant kingdom.

The symbiosis of plants with AM fungi is so crucial for plant growth on land that about 80% of land plants engage in it (4). The plant allows AM fungi to enter its roots and form nutrient exchange structures called arbuscules in its cells (see the figure). Outside the root, the fungal hyphae grow into the soil, up to 30 cm from the plant root, where they

Lipid biosynthesis and transfer are not the only evolutionarily conserved processes that occur in *M. paleacea* upon colonization by AM fungi. Rich *et al.* also report orthogroups of genes involved in strigolactone biosynthesis that show a conserved response across the plant kingdom, including in *M. paleacea*. Strigolactones are rhizosphere signaling molecules that have been shown to play a key role in the colonization of roots by AM fungi (6) and are regularly claimed to have been instrumental for terrestrialization (7) (see the figure). Rich *et al.* do not go into detail on these genes, but it can be safely assumed that they refer to *CAROTENOID CLEAVAGE DIOXYGENASE 8a* and *8b* (*CCD8a* and *CCD8b*). The enzyme

Plant Hormone Biology Group, Swammerdam Institute for Life Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, Netherlands. Email: h.j.bouwmeester@uva.nl

Tanking up energy through atypical charging

Bo HuT. Leo Liu

Science, 372 (6544), • DOI: 10.1126/science.abi5911

View the article online

<https://www.science.org/doi/10.1126/science.abi5911>

Permissions

<https://www.science.org/help/reprints-and-permissions>