Aqueous batteries get energetic

Aqueous batteries hold promise for large-scale energy storage, but are often maligned because of their low energy densities. Now, a demonstration of halogen conversion–intercalation chemistry inside graphite has blazed a trail for high-energy aqueous batteries.

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Batteries that use aqueous electrolytes can be cheap and safe; however, they normally suffer from low energy densities because they are restricted by the narrow electrochemical stability window of water, which theoretically is 1.23 V — go over that and you can electrolyse it. In 2015, Wang, Xu and co-workers introduced the ‘water-in-salt’ electrolyte, in which hydrated ions outnumber free water molecules. This new family of electrolytes, compared to the conventional dilute aqueous electrolytes, transforms the chemical environment of water by fastening water molecules in the solvation shells of the ions. Such aqueous electrolytes, with very few free water molecules, not only expand the electrochemical window considerably, but also provide conditions conducive to exploring novel redox chemistries that were otherwise not viable in non-aqueous electrolytes or dilute aqueous electrolytes. Now, writing in Nature, Wang, Xu and co-workers describe a battery that functions using both the conversion and intercalation of halogen atoms inside graphite, a newly discovered anionic redox phenomenon.

State-of-the-art battery technologies use the intercalation of lithium ions into transition-metal-oxide cathodes and graphite anodes. However, in an attempt to improve battery energy density, there has been much recent interest in the use of conversion chemistry electrodes, that is, those that use chemical-bond forming or breaking reactions, rather than those that simply intercalate and host ions with minimal bonding variation. Wang, Xu and co-workers have now developed a battery that uses both. The electrode chemistry is facilitated by a ‘water-in-bisalt’ gel electrolyte and gives rise to a high energy density, rivalling the state-of-the-art Li-ion batteries.

To create the cathode for their battery, Wang, Xu and co-workers mixed solid LiBr and LiCl with graphite. The cathode undergoes a two-stage process on charge and discharge and they have defined this new electrode chemistry as a ‘conversion–intercalation’ mechanism. During battery charge, bromide and chloride ions in LiBr and LiCl are consecutively ‘converted’ into their nearly neutral atomic states: Br–0.05 and Cl–0.25, and intercalated into graphite galleries (the gaps between the graphene layers of carbon atoms; Fig. 1a). The following reversible redox reactions take place inside the graphite:

\[
\text{LiBr} + C_n \leftrightarrow C_n[Br] + Li^+ + e^- \\
(4.0 - 4.2 \text{ V})
\]

\[
\text{LiCl} + C_n[Br] \leftrightarrow C_n[BrCl] + Li^+ + e^- \\
(4.2 - 4.5 \text{ V})
\]

The operation of the graphite cathode seems to resemble that of the recently developed dual-ion batteries, such as the dual-graphite battery. In a dual-graphite battery, the graphite cathode functions as an acceptor-type graphite intercalation compound by hosting molecular anions, for example, PF$_6$$^-$ and TFSI$^-$ (ref. 1). However, the battery described by Wang, Xu and co-workers differs from the dual-graphite battery — which works solely through intercalation — as the role of bromide and chloride ions in this case is more about being redox centres rather than charge carriers.

When looking at the operation of this battery chemistry, the charge process releases lithium ions from the cathode into the electrolyte, and concurrently electrolyte-born lithium ions are intercalated into the graphite anode. Indeed, this battery is a ‘rocking chair’ battery, where lithium ions commute between the two electrodes during charge and discharge processes.

The anionic redox-activity of the cathode is made possible by the unique water-in-bisalt gel electrolyte. The water molecules in this electrolyte are anodically stable up to 4.9 V versus Li$^+/Li$, thus providing a high potential ceiling to allow the reversible oxidation of chloride and bromide to their near-neutral oxidation states. Another advantage of this electrolyte is that the LiCl and LiBr salts in the cathode become their solid hydrates on contact with the water-in-bisalt gel electrolyte; nevertheless, the
The chemical functionality necessary for the origin of life may have emerged from simple reactions assembled into complex networks. Now, it has been shown that prebiotically relevant heterogeneous reaction networks can generate robust oscillations within complex mixtures comprised of precursors that do not oscillate on their own.

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All living organisms have natural rhythm — circadian clocks, endogenous physiological timing systems that generate 24-hour oscillations in anticipation of dusk and dawn, are a well-known example. One of the challenges in contemporary origin of life and systems chemistry research is to mimic such functions using simple synthetic molecular networks\(^1,2\). This is particularly true for systems that are out of chemical equilibrium and show complex dynamic behaviour, such as multi-stability, oscillations and chaos. In addition to realizing new concepts and synthetic challenges, these studies may shine light on the origin of function in early chemical evolution, prior to the first appearances of life. It is likely that molecular functions at these early stages arose without efficient enzyme catalysis or nucleic acid templating. Furthermore, the chemical pathways facilitating such functions may 'compete' for resources with other pathways, and their yields might be hindered when multiple products are formed in the mixtures. It has been proposed\(^3\), however, that in some cases phase transitions can take place in 'messy' prebiotic mixtures and bring about efficient functions not found in the much simpler systems where the individual processes take place.

Now, in a new paper in the *Journal of the American Chemical Society*, George Whitesides and colleagues reveal an interesting, even counterintuitive, observation: that prebiotically relevant heterogeneous reaction networks — formed from mixtures of the precursors for several oscillating reactions — can generate collective behaviour\(^4\). In particular, the team demonstrate that oscillations can occur in complex mixtures of precursors that would not produce oscillations on their own. They also reveal that these heterogeneous mixtures are better able to withstand changes in reaction conditions than homogeneous systems.

The systematic design of a chemical oscillator typically requires the selection of a reaction that produces its own catalyst — an autocatalyst or activator that serves as a positive feedback — and an inhibitor species that removes the activator in a negative feedback loop (Fig. 1a). These reactions, performed under flow conditions that maintain the system far from equilibrium, may display four different types of behaviour: either high or low activator steady states, a bistable switch ('memory') can serve as a unique extension of the current collector that fixes and protects the 'plated' halogen atoms. Furthermore, looking at the bigger picture, the value of the electrochemical synthesis of \(\text{C}_2\text{Al}_0\text{Br}_0\text{Cl}_0\) goes well beyond batteries. This reported battery is an example of a powerful reactor to synthesize new compounds that may transcend the interests of different disciplines.

**Rhythm before life**

**SYSTEMS CHEMISTRY**

**References**