Editorial

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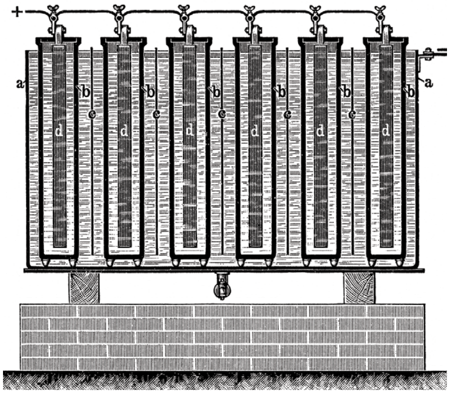
Decoupling and recoupling electrochemical reactions

This Editorial highlights recent strategies for bridging electrochemical half-reactions that have been deliberately separated into distinct environments, showcasing how creative recoupling approaches can unlock improved performance and new chemistries beyond the reach of conventional cell designs.

Electrochemical cells tie oxidation and reduction together: current flowing through the external circuit requires both half-reactions to proceed at matching rates, linked through a shared electrolyte that maintains charge balance. In principle, this coupling is elegant. Each electrode can produce valuable products while the system stays self-regulated. In practice, though, it is uncommon for two desired reactions to thrive in the same environment. As a result, one half-reaction typically drives the cell design, while the other plays a secondary role (oxygen bubbles off the anode as an unwanted by-product, or a sacrificial metal dissolves simply to close the circuit).

Paired electrolysis, in which both electrodes produce commercially useful outputs, is the exception. The chlor-alkali process, which yields chlorine gas at the anode and sodium hydroxide at the cathode, is one of the most celebrated examples[1]. But at the same time, the continued prominence of a process discovered in the late nineteenth century is itself evidence that successful pairing relies on a rare compatibility of conditions that most target chemistries do not share.

A growing body of work now seeks to resolve this tension by separating the two half-reactions (spatially and/or temporally) into independently optimizable electrochemical components, which are then strategically recoupled to preserve the electrical and ionic linkages that allow the overall process to function[2]. These designs are enabled by innovations at the interface between the now-decoupled half-reactions, including redox mediators that shuttle charge between compartments, reservoir electrodes that store and release ions on demand, and unconventional membranes that permit only the desired ionic species to pass.



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The design landscape for such decoupled but paired systems is, in principle, definitionally broader than that for traditional cell architectures. Ongoing and potential applications span energy storage, electrosynthesis and chemical separations; in this Editorial, we spotlight a Research Article and Comment from this month's issue that explore innovations in this space at both the electrochemical-cell and system levels.

First, an Article by Yi Cui and co-workers reconceptualizes what a proton-exchange membrane can be by abandoning proton conduction through polymers altogether in favor of a hydrogen-mediated transport pathway. Rather than relying on conventional polyelectrolyte membranes, for which the conductivity–selectivity trade-off has long limited performance, the authors introduce a membrane architecture in which protons are converted to hydrogen gas on one side, diffuse through a gas chamber and are re-oxidized to protons at a second electrode. This design fully eliminates any direct ionic channel between the electrolytes.

Aided by the rapid diffusion of hydrogen gas, the high electrical conductivity of the metal (in this case, Ti foil) and the fast reaction kinetics, the cell achieves nearly 100% proton selectivity, enabling the stable separation of electrolytes with vastly different pH values while maintaining area-specific resistances comparable to commercial membranes. The authors go on to demonstrate the membrane's utility in pH-decoupled Zn–MnO_2 batteries and in acid–base generation from artificial seawater, highlighting how this gas-mediated transport pathway could potentially overcome a decades-old materials constraint in ion-exchange-membrane design.

Through this expanded design landscape, the advances potentially enabled by decoupled paired electrochemistry can extend beyond improved selectivity and efficiency at the cell level. As discussed in a Comment by Song Jin and co-workers, these architectures can eliminate energy-intensive intermediate separation steps, pair otherwise incompatible redox couples (such as those requiring vastly different solvent types), and enable modular designs in which anodic and cathodic production can be scheduled independently. As an example, the authors describe how a redox reservoir based on a proton-ion-battery material with fast kinetics can couple electrochemical half-reactions operating at different rates to participate in frequency-regulation markets with second-level response times, creating promising opportunities for integrating electrochemical production with intermittent renewable power[3].

The ability to decouple and recouple half-reactions at will reframes electrochemical cell design as an optimization problem with new degrees of freedom. As electrochemistry continues to expand into grid-scale energy storage, distributed chemical manufacturing and seawater processing, among other applications, the demand for creative bridging strategies will only intensify. The work highlighted here suggests that the most impactful innovations ahead lie not only in the electrochemical reactions themselves, but also in the space between them — the membrane, mediator or relay that holds two otherwise independent electrochemical worlds in balance.

References

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