

SPEEK scaling UP

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In this new issue of *Joule*, Xianfeng Li and colleagues demonstrated the pilot scale roll-to-roll synthesis of sulfonated poly(ether ether ketone) (SPEEK) membrane and the scaling up of zinc flow batteries (ZFBs) stack 300–4000 W with membrane area up to 3 m². Compared to expensive Nafion membranes (\$500–1500 m⁻²), cost analysis demonstrated the significant cost reduction of SPEEK membranes to \$12 m⁻² and subsequently enormous cost reduction of flow battery stacks. This cost reduction will advance the manufacturing of flow battery systems for large-scale energy storage plants.¹

Human economic and subsistence activities cannot exist without energy. With rapid societal development, energy demands have significantly increased as well. Based on worldwide efforts toward sustainable development, renewable energy is becoming an important energy source worldwide. In the 21st century, wind and solar have become fast-growing renewable energy sources. However, the integration of renewable energy systems is highly restricted by solar and wind's inherent intermittency. Specifically, wind energy is most intense during nighttime. However, the peak demand for electricity is during the day. On the other side, solar energy is highly dependent on sunlight, which varies between day and night, throughout seasons, and based on location. Therefore, the efficient application of renewable energy requires a consistent, efficient, and cost-effective large-scale energy-storage system to store energy when there is high harvesting but low demand and provide energy when there is high demand but low harvesting. **Figure 1** shows the integration of renewable energy systems, including renewable energy harvesting from solar or wind, large-scale energy storage systems, power grids, and city/industrial consumers, which are all connected by a central controller. The central controller works smartly to distribute energy according to the energy supply or

demand and balance the load in the power grid.

Owing to advanced merits of tunable capacity and power, long lifetime, and high safety, aqueous flow batteries have become one of promising technologies for large-scale energy storage systems. Among them, the aqueous Zn-based flow batteries (ZFBs) are becoming outstanding applications because of low cost and redox potential of zinc, environmental friendliness, and the elimination of electrolyte volume. However, in the presence of Zn²⁺, an anion exchange membrane (AEM) loses ion conductivity due to side reaction and Zn deposition, while a cation exchange membrane (CEM) usually results in poor anion conductivity due to electrostatic interaction between anion and cation exchange groups. Consequently, in the aqueous ZFBs, poor reversible capacity and energy conversion efficiency are obtained, especially at high current density. To date, there are relatively few attempts to apply hydrocarbon-based CEMs in novel alkaline battery systems in a laboratory scale. This work done by Li and colleagues demonstrates the high hydroxide conductivity of sulfonated poly(ether ether ketone) (SPEEK) membranes, which are usually used as CEMs, in alkaline battery systems. Although CEMs with anion groups (sulfonate groups) are capable of trans-

porting cations in alkali, they have rarely been applied in alkaline-based systems for anion exchange.

Membranes in flow batteries block the active materials but allow ions to pass across to compensate for the electrochemically generated charges and maintain neutrality for the whole system (**Figure 2**). In order to obtain high coulombic efficiency, high energy efficiency, and high durability, the membrane need to have high selectivity, high ionic conductivity, high mechanical strength, high chemical stability, and low crossover.² Perfluorinated ion exchange membranes are widely used in vanadium flow batteries and other aqueous flow batteries systems because of their ion selectivity, high conductivity, and outstanding durability, but their cost is prohibitively high due to the complicated synthesis and manufacturing process, which accounts for up to 20–40% of the overall cost of vanadium flow battery systems and significantly prevents wider market penetration of flow battery systems.

There are two major kinds of membranes: ion exchange membranes and porous membranes.³ Porous membranes transport ions through channels or pores. For the ion exchange membrane, there are primarily two ion transfer mechanisms: Grotthuss mechanisms and vehicle mechanisms.⁴ The nuclear magnetic resonance experiments indicated that the transport of OH⁻ in this SPEEK membrane under alkaline medium followed Grotthuss mechanisms, which endowed the membrane with high ionic conductivity. More specifically, in alkaline media, the oxygen-containing species such as H₂O and OH⁻ were confined in the SPEEK

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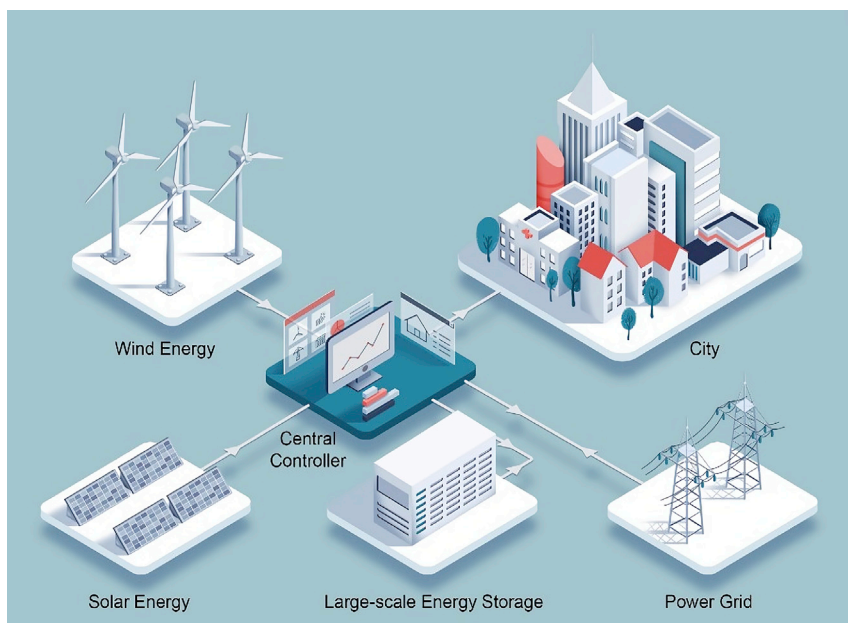


Figure 1. Renewable energy-system integration: Power generation, energy storage systems, and power transmission/distribution

membrane, forming a continuous hydrogen-bond network. The continuous hydrogen-bond network enabled the fast dissociation of proton in H-O-H (H₂O) and the transfer from the H₂O to adjacent OH⁻ through the Grotthuss mechanism.

The SPEEK membranes demonstrated superior stability and conductivity under alkaline medium after treatment in a 5 mol L⁻¹ NaOH solution at 60°C for 41 days, after which the membrane still enabled a stable alkaline zinc-iron flow battery performance for more than 650

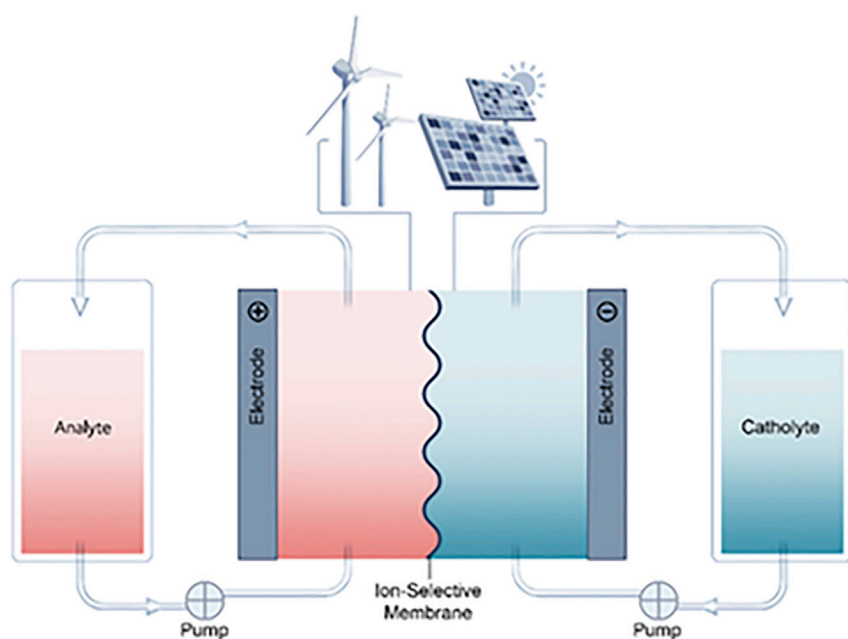


Figure 2. Schematic diagram of redox flow batteries and important indicators of the membrane

cycles. The U.S. Department of Energy's (DOE) Energy Earthshots Initiative aims to accelerate breakthroughs of more abundant, affordable, and reliable clean energy solutions within the decade. Achieving the Energy Earthshots will help us tackle the toughest remaining barriers to addressing the climate crisis and more quickly reach the goal of net-zero carbon emissions by 2050 while creating good-paying union jobs and growing the clean energy economy. This work illustrated a potential pathway for manufacturing and scaling up of next-generation cost-effective flow batteries based on low-cost hydrocarbon membranes developed in past decades to translate to large-scale applications for grid energy storage.

Distributed stationary storage holds great promise to impact the energy landscape by increasing renewable deployment, improving grid stability and efficiency, reducing dependence on imported fuels, and facilitating electric vehicle charging. The flow battery systems represent an outstanding scientific and technical opportunity to address this challenge. Unlike traditional batteries, active materials are dissolved in the electrolyte solutions in flow batteries, circulating through the positive and negative electrode compartments for energy conversion, decoupling power and energy, easing of scale up, and achieving greater safety. Additionally, the membrane in the flow batteries plays a decisive role in ion transportation and reducing crossover to obtain high coulombic efficiency and energy efficiency. However, despite rapid progress and recent demonstrations of pilot scale flow batteries systems—including vanadium flow batteries, all iron flow batteries, and zinc bromide—the level of manufacturing capability for flow batteries systems is currently insufficient to meet the expected demand for stationary grid storage, which contributes to a prohibitively high cost for the overall systems. A particularly good feature of this work is the demonstration of the

scale up of this technology and that this redox flow batteries may be feasible as a solution to electrical power storage. Furthermore, there is a comprehensive cost analysis, since cost will be one of the primary determining factors in the adoption of redox flow batteries for storage. While the advantages of this work are clear, further efforts are needed to develop long-duration energy storage. The DOE long-duration

energy storage grand challenge roadmap clearly defines “long-duration” as >10 h.

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Electrochemical CO₂ separation by a shorted membrane

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Owing to the alkaline environment, anion-exchange membrane fuel cells allow employing cost-efficient components, but also suffer from the electrolyte carbonation induced by the CO₂ in the air feed. Recently in *Nature Energy*, Shi et al. introduced an anion- and electron-conductive membrane for efficient electrochemical CO₂ removal, providing a potential solution.

The unstable and depleting fossil energy as well as the accompanying environmental degradation have stimulating intensive demand for clean, efficient, and renewable energy technologies.¹ Benefiting from the moderate working conditions, zero emissions, efficient energy-conversion rates, high power densities, and reproducible fuel resources, hydrogen-based low-temperature fuel cells (FCs), which mainly include two types based on proton- and anion-exchange membranes (PEMs and AEMs), are widely considered as one of the most promising alternatives to traditional fossil-energy technologies.² However, under the harsh acidic conditions, PEMFCs rely heavily on expensive Pt-based electrocatalysts and other anticorrosive components for both facilitating the cathodic oxygen reduction reaction

(ORR) and gaining a sufficient durability.^{1,3,4} In comparison, the more benign alkaline environment in AEMFCs enables the use of cheaper non-Pt or even nonprecious-metal electrocatalysts, nickel-based bipolar plates, and other components, making AEMFCs easier to meet the cost requirement for commercialization.⁵

Although very appealing, one major factor stagnating the practical applications of AEMFCs is the electrolyte carbonation caused by the CO₂ in the air feed, in which carbonates are formed via the reaction of CO₂ and hydroxide anions at the cathode.⁶ These carbonates can evidently reduce the ionic conductivity of the membrane, and more importantly, accumulate at the anode to form a pH gradient between the two electrodes, thus

increasing the CO₂-related overpotential at the anode, which eventually lead to an output voltage loss.⁶ Therefore, removing the CO₂ from the air feed in advance is critical to the cell performance of AEMFCs.

In general, there are two traditional methods for removing CO₂ from mixed gases:⁷ (1) the amine scrubbing, which uses amine-based solvents to absorb CO₂ and regenerates via a temperature or pressure swing and (2) the irreversible sequestration, which uses alkaline aqueous solutions or solid sorbents to permanently capture CO₂. Unfortunately, none of the two methods can simultaneously meet the cost-efficient, energy-saving, and system-compact requirements of the AEMFCs in many practical applications. For the past few years, the electrochemical CO₂ separation, which selectively removes CO₂ from mixed gases using electrochemical reactions as the driven force, has again attracted increasing attention because of some encouraging developments in both energy consumption and

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