

A Highly Ion-Selective Zeolite Flake Layer on Porous Membranes for Flow Battery Applications

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Abstract: Zeolites are crystalline microporous aluminosilicates with periodic arrangements of cages and well-defined channels, which make them very suitable for separating ions of different sizes, and thus also for use in battery applications. Herein, an ultra-thin ZSM-35 zeolite flake was introduced onto a poly(ether sulfone) based porous membrane. The pore size of the zeolite (ca. 0.5 nm) is intermediary between that of hydrated vanadium ions (> 0.6 nm) and protons (< 0.24 nm). The resultant membrane can thus be used to perfectly separate vanadium ions and protons, making this technology useful in vanadium flow batteries (VFB). A VFB with a zeolite-coated membrane exhibits a columbic efficiency of > 99 % and an energy efficiency of > 81 % at 200 mA cm⁻², which is by far the highest value ever reported. These convincing results indicate that zeolite-coated membranes are promising in battery applications.

Flow batteries are receiving wide attention for their potential in electrochemical energy storage because they present a perfect combination of qualities, such as high efficiency, high reliability, a long life cycle, and cost effectiveness.^[1] In contrast to other secondary batteries, flow batteries store energy in electrochemically active materials, where at least one of the materials is dissolved in circulated flowing liquid electrolytes. Electrolytes are flowed cyclically from storage tanks to electrodes, where chemical energy is converted into electrical energy or vice versa.^[2] Since the 1970s, numerous kinds of flow battery systems, including

those comprising iron/chromium (vanadium) (Fe/Cr(V)), vanadium, and zinc/bromine (Zn/Br), have been widely investigated and are currently at the demonstration stage.^[3] Recent research on flow batteries (aqueous or non-aqueous) focuses on development of redox-active materials that can affordably translate to high-energy-density batteries. On the basis of energy-density considerations, several kinds of flow batteries have been designed and fabricated for potential use in energy storage applications, including zinc polyiodide,^[1b] lithium-iodine solar,^[4] and non-aqueous lithium-iodine/TEMPO flow batteries.^[5]

Both traditional aqueous and recently developed non-aqueous flow batteries contain an ion exchange membrane that is responsible for transferring non-reaction ions (such as H⁺, Na⁺, Li⁺ and SO₄²⁻). The membrane allows completion of an internal circuit as well as separation of the positive and negative electrolytes, which are kept in separate storage tanks.^[6] The properties of the ion exchange membrane greatly affect the performance of flow batteries. To minimize power losses and resistance, the membrane is required to ensure a high ionic conductivity and selectivity (the transport of active species must be minimized to avoid cross-contamination of the active species and to reduce energy and capacity losses).^[7] Membranes should also possess certain qualities, such as good chemical stability and low cost, because most flow batteries are operated under strongly acidic and oxidizing conditions. Both cation and anion exchange membranes coupled with porous membranes have been investigated for flow battery applications. Among these, perfluorinated cation membranes (Nafion) are commonly used in flow battery systems (vanadium, Fe/Cr(V) and zinc-polyiodide flow batteries for example)^[1a,2] and often exhibit excellent chemical stability and ion conductivity. However, extremely high cost and undesirable crossover of active species limits further application. Sulfonated or quaternized polyaromatic ion exchange membranes have the advantages of high ion selectivity and low cost, but they often suffer from poor chemical stability of their ion exchange groups in the extremely acidic and oxidizing media of flow batteries, particularly in the case of VFBs.^[8] Thus, there is an urgent need to develop high-quality and low-cost membranes to achieve cost effective flow battery systems.

Porous membranes, based on the idea of separating redox-active ions from non-reaction ions by pore size exclusion, have been widely accepted as promising materials for use in flow batteries.^[2,9] The concept was verified by a VFB,^[9b,10] where separation of vanadium ions and protons was realized by pore size exclusion. However, the selectivity and conductivity of membranes still need improvement because the pores of currently explored membranes are usually asym-

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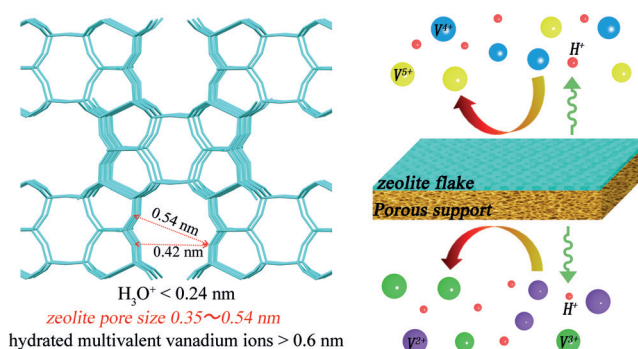
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metric. The selectivity of membranes is normally ensured by multiple exclusions arising from highly curved pores, which induce relatively high ion resistance. Furthermore, the ion transport mechanism through membranes is very complicated because of the functionality of the curvature pores (charge density and hydrophilicity for example). Critically, porous membranes require pore sizes lying in between that of redox-active ions and non-reaction ions (such as H^+ , Na^+ , Li^+ and SO_4^{2-}), which can isolate active species effectively, allow free transport of non-reaction ions, and enable pore size exclusion simultaneously.

Zeolites, a class of crystalline aluminosilicates, are ion conducting, hygroscopic, and microporous materials (with pore sizes between 0.3 and 1 nm) that have been targeted for applications requiring selective membranes, chemical sensors, and as components in micro-electronic devices.^[11] Zeolite frameworks, formed by interlinked SiO_4 and AlO_4^- tetrahedra, contain large numbers of exchangeable cations (Na^+) located at AlO_4^- sites. These cationic sites can be easily exchanged for H^+ or Li^+ , allowing installment of a high number of very strong acid sites and affording good ion conductivity.^[11b,12] Moreover, the multidimensional and tunable channel networks provided by zeolites allow precise and accurate control of pore sizes for inclusion of a range of hydrated metal ions with diverse radii, while also allowing different ions in aqueous solutions to be well separated. Considering the differences between Stokes radii of redox-active ions and non-reaction ions, zeolites thus hold potential in flow battery applications. Herein, we demonstrate that membranes based on microporous zeolites can overcome the aforementioned challenges facing flow battery applications, while providing excellent ion selectivity, conductivity of non-reaction ions with good rate properties, and cycling efficiency.

Our proof-of-concept studies are based on VFBs, the most competitive candidates for cost effective energy storage devices, intended for wind and solar power systems and large-scale electric grids.^[1a,14] ZSM-35 was deliberately selected as a zeolite scaffold owing to its appropriate pore size (0.42 nm $\times$ 0.54 nm for 10-ring apertures and 0.35 nm $\times$ 0.48 nm for 8-ring apertures),^[15] which is in the range between the Stokes radii of protons (0.24 nm for H_3O_2^+ , an in situ form of H_3O^+)^[16] and hydrated multivalent vanadium ions (>0.6 nm).^[17] Our materials are critically different from traditional zeolite separators, where zeolites are generally grown on a porous support such as α -alumina, large ohmic resistance is likely to be involved, and the materials produced are fragile.^[13b,18] Our approach is to construct a selective layer using spray coating to deposit size selective zeolite crystals onto a porous support, thereby forming a composite membrane (Scheme 1).^[19]

To realize this idea, a porous poly(ether sulfone) (PES) based membrane was selected as the support, which was prepared by phase inversion using SPEEK (sulfonated poly(ether ether ketone)) to tune the pore size and distribution of each membrane. Pores were kept relatively large to ensure membrane conductivity.^[20] A zeolite flake was then sprayed uniformly onto the prepared membrane. A typical surface and cross-sectional view of pristine substrate is presented in Figure 1 a,c, where a dense surface morphology



Scheme 1. Design principles of a VFB with a porous membrane bearing a zeolite flake layer.

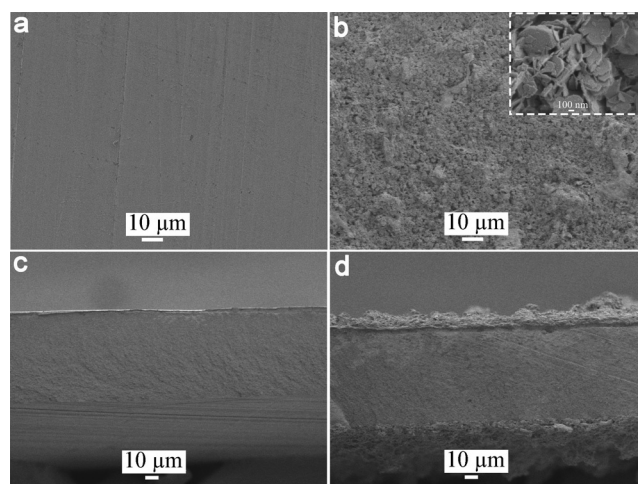


Figure 1. Surface and cross-section morphology of membranes; a) and c) surface and cross-section morphology of a pristine porous support; b) and d) surface and cross-section morphology of a zeolite-coated membrane. The inset in (b) shows the morphology of zeolite particles on the porous support.

and porous cross-section can be observed distinctly (Supporting Information, Figure S1 c). After coating, the dense surface was covered with zeolite particles (Figure 1 b), which appear as long hexahedral crystals with lengths between 1–1.5 μm (Supporting Information, Figure S1 a and Figure S2 a).^[21] The thickness of the zeolite flake layer on the membrane was about 8 μm (Figure 1 d; Supporting Information, Figure S1 b,d) with a Na:O:Si:Al molar ratio of 0.35:77.62:20.78:1.24 (Supporting Information, Figure S2 c), indicating that a large number of exchangeable cations exist in the framework. Before these characteristics can be considered, a crucial requirement of zeolites implemented in flow batteries needs to be satisfied. Namely, their stability in the extreme chemical environment of the anolyte, which contains strong acid (3 mol L⁻¹ H_2SO_4) and strongly oxidizing VO_2^+ ions. Both chemical agents are highly corrosive to a wide range of materials.^[6a] To confirm the stability of the zeolite, ZSM-35 particles were immersed in a 1.5 mol L⁻¹ VO_2^+ solution acidified with 3 mol L⁻¹ H_2SO_4 at room temperature for 24 h. The material was subsequently examined by scanning electron microscopy (SEM; Supporting

Information, Figure S2 a,b), energy dispersive X-ray spectroscopy (EDS; Supporting Information, Figure S2 c,d) and X-ray diffraction (XRD; Supporting Information, Figure S3). Compared to the initial zeolite, no appreciable changes in crystal phase, size, and shape, or Si/Al ratio were observed, indicating that ZSM-35 has good stability in a VFB medium.

The morphology and pore structure of ZSM-35 was verified by TEM and HRTEM images (Figure 2). The image (Figure 2b) viewed in the [010] direction, together

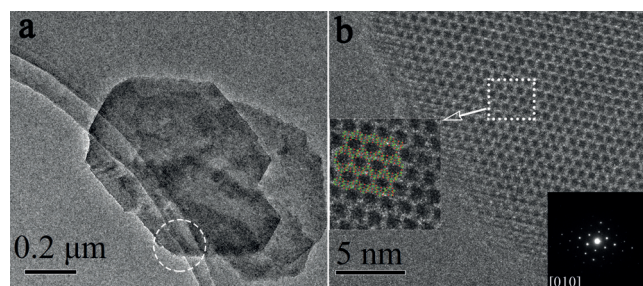


Figure 2. a) TEM image of ZSM-35 zeolite; b) HRTEM image of ZSM-35 zeolite viewed in the [010] direction. The inset shows that a ZSM-35 framework drawn by diamond 4.0 (section in color: viewed in the [010] direction) fits perfectly with an HRTEM image viewed in the [010] direction. HRTEM images were collected on an FEI Tecnai G² F30S-Twin microscope, 300 kV.

with XRD data, confirmed the ordered microporous structure of ZSM-35. Pore size estimated from the HRTEM image was approximately 0.5 nm, with a narrow distribution range, which is consistent with that determined from the Ar sorption isotherm data (Supporting Information; Figure S4). This pore size fits perfectly into the range between the Stokes radius of protons (< 0.24 nm) and hydrated multivalent vanadium ions (> 0.6 nm), allowing perfect separation of protons and multivalent vanadium ions by pore size exclusion. Thus, it is expected that ZSM-35 will yield composite membranes with very high selectivity and proton conductivity.

An ion diffusion measurement was carried out to confirm the selectivity of the zeolite flake based porous membrane. A linear relationship between time and ion concentration in the right cell (containing 1.5 M MgSO₄ and 3 M H₂SO₄; Supporting Information, experimental part) is illustrated in Figure 3.

The ion permeation rate was calculated from the slope of the line according to Fick's diffusion law.^[6b] The proton to VO²⁺ permeation selectivity of the zeolite-coated membrane was 44 300 ($\alpha_{H/V}$ was obtained from the ratio between the H⁺ slope in Figure 3b and the VO²⁺ slope in Figure 3a), which is more than 1000 times higher than that of Nafion 115 ($\alpha_{H/V}$ = 35.002) and the substrate ($\alpha_{H/V}$ = 17.630). The ultrahigh selectivity of the zeolite-coated membrane, which results from the pore size exclusion of the zeolite flake, suggests that our concept of zeolite separation processes will be highly applicable to flow batteries.

To investigate electrochemical performance, the zeolite-coated and pristine substrate membranes were employed to assemble VFB single cells. For comparison, the electrochemical performance of Nafion 115 was also measured. The area

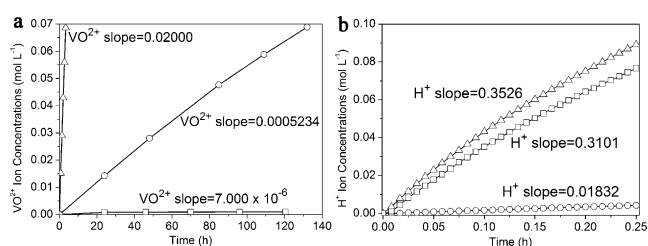


Figure 3. a) VO²⁺ concentration and b) H⁺ concentration versus time at the diffusion side of a diffusion cell using substrate, Nafion 115 and zeolite-coated membranes. Key: substrate (—Δ—), zeolite-coated membrane (—□—), Nafion 115 membrane (—○—).

resistance of these membranes (substrate, Nafion 115 and zeolite-coated membranes) was measured by electrochemical impedance spectroscopy prior to a cycling test. The substrate porous membrane showed an area resistance of 0.37 Ω cm⁻², while the zeolite-coated membrane showed an area resistance of 0.61 Ω cm² (still lower than Nafion 115 at 0.98 Ω cm⁻²; Supporting Information, Figure S5). These results imply that zeolite coating does not cause much higher impedance and a VFB using pristine substrate or zeolite-coated membranes will have a lower ohmic loss than Nafion 115. Accordingly, the charge and discharge voltage profiles shown in Figure 4a (obtained at the fourth cycle with a current density of 80 mA cm⁻²) suggest that batteries with pristine substrate and zeolite-coated membranes exhibit a lower overpotential than that of the battery with a Nafion 115 membrane. Also observed in the voltage profiles was a large difference

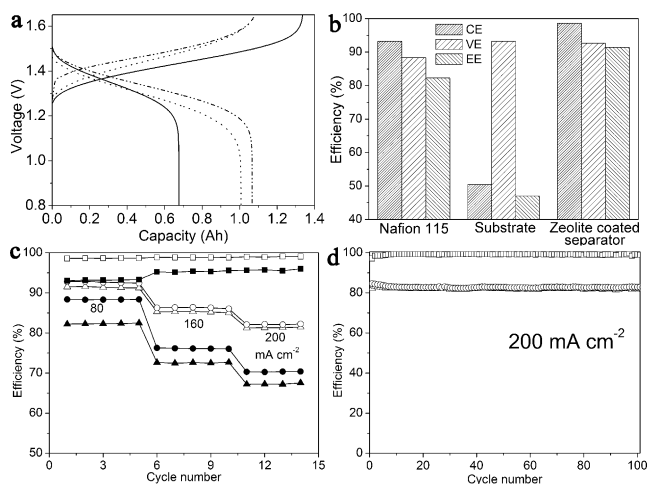


Figure 4. Battery performance of prepared membranes. a) Charge–discharge voltage profiles of batteries with substrate, Nafion 115 and zeolite-coated membranes at a current density of 80 mA cm⁻². Key: substrate (—), zeolite-coated separator (—□—), Nafion 115 membrane (—••••). b) The performance of a VFB assembled with substrate, Nafion 115 and zeolite-coated membranes at a current density of 80 mA cm⁻². c) The cycling performance of a VFB using Nafion 115 and zeolite-coated membranes with current densities ranging from 80–200 mA cm⁻². d) The charge–discharge cycling performance of a VFB with a zeolite-coated membrane at 200 mA cm⁻². Zeolite-coated separator: coulombic efficiency (—□—), energy efficiency (—Δ—), voltage efficiency (—○—). Nafion 115 membrane: coulombic efficiency (—■—), energy efficiency (—▲—), voltage efficiency (—●—).

between the charge and discharge capacity of the VFB containing a zeolite-coated membrane compared to the VFB with a substrate membrane, indicating a much lower degree of self-discharge for the zeolite-coated membrane as a result of the ion-selective zeolite crystals layered onto the substrate (Figure 3a). Furthermore, a VFB using a zeolite-coated membrane showed a higher discharge capacity and a similar charge capacity compared to a VFB with a Nafion 115 membrane, indicating that the zeolite-coated membrane achieves improved ion selectivity (as proven by vanadium permeability, Figure 3, and a long self-discharge duration; Supporting Information, Figure S6). This means that the zeolite flakes separate vanadium ions and protons effectively.

The low area resistance and vanadium permeability of zeolite-coated membrane (Figure 3a) combines excellent proton conductivity (Figure 3b; attributed to exchangeable cations located at the AlO_4^- sites) and ion selectivity (appropriate pore size). The membrane is consequently expected to achieve an outstanding performance in VFB. As shown in Figure 4b, a VFB using a substrate porous membrane produced a columbic efficiency (CE) of 50.39%, a voltage efficiency (VE) of 93.28% and an energy efficiency (EE) of 47.00% at a current density of 80 mA cm^{-2} . In comparison, a very high CE of 98.63% was obtained with zeolite-coated membrane, indicating that the shape selectivity of the thin zeolite flakes gives rise to a much lower vanadium permeability. A slightly lower VE (92.68%) was also observed, proving that the thin flake coating of ZSM-35 zeolite does not significantly affect proton conductivity. As a consequence, a VFB with a zeolite-coated membrane shows an EE of 91.41%, which is by far the highest value ever reported. Compared with Nafion 115 membrane (CE of 93.19%, VE of 88.31% and EE of 82.30% at a current density of 80 mA cm^{-2}), the zeolite-coated membrane shows an exceptionally high efficiency overall, clearly outperforming perfluorinated membranes. Moreover, a VFB using the zeolite-coated membrane shows much higher CE and VE than a VFB using a Nafion 115 membrane under comparable operating conditions, with current densities ranging from 80 to 200 mA cm^{-2} (Figure 4c). The battery with a zeolite-coated membrane achieves a CE of 98.82% and an EE of 85.25% under 160 mA cm^{-2} , which is much higher than that of the battery using a Nafion 115 membrane (CE of 95.32% and EE of 72.58% under 160 mA cm^{-2}). Remarkably, a VFB with a zeolite-coated membrane is able to maintain an EE of 81.34% even at a high current density of 200 mA cm^{-2} . Such exceptional results have never been reported. This high rate capacity, which is one of the key parameters used to evaluate the merits of a VFB system, is mainly attributed to the high proton diffusion and shape selectivity attributes of the thin zeolite flake.^[22]

Further to the excellent electrochemical performance described, a VFB using a zeolite-coated membrane exhibited much better capacity retention than that bearing Nafion 115 (Supporting Information, Figure S7). Capacity decay over cycling is a vital issue facing VFBs that employ Nafion 115, which results because of hydrophilic water channels of about 2.5 nm diameter through which vanadium ions can be easily transported and subsequent imbalanced self-discharge reac-

tions promoted.^[23] Continuous capacity decay constitutes one of the major barriers hindering commercialization of flow batteries. In this regard, zeolite-coated membranes are better at maintaining stable capacity over cycling, and should allow a VFB system to deliver energy consistently with minimal system maintenance.^[22a]

Stability in extremely acidic and oxidizing environments is a crucial requirement of membranes implemented inside flow batteries. As described herein, a battery with a zeolite-coated membrane demonstrated excellent battery performance after continuously running more than 100 cycles at current densities of 80 mA cm^{-2} (Supporting Information, Figure S8) and 200 mA cm^{-2} (Figure 4d). Remarkably, the battery operated without a decay in efficiency, and retained good chemical stability of both the porous substrate and the ZSM-35 zeolite layer. Moreover, the zeolite layer remained unchanged after continuous operation for more than 100 cycles at 200 mA cm^{-2} (Supporting Information, Figure S9b,c), indicating that the zeolite-coated membrane possesses very good stability. Additionally, no obvious change could be found in the zeolite-coated membrane during an oxidative stability test (Supporting Information, Figure S9a), further confirming the stability of the prepared zeolite-coated membrane.

The temperature-dependent behavior of the zeolite-coated membrane was also evaluated using charging and discharging experiments at different temperatures (varying from -5°C to 50°C at a current density of 80 mA cm^{-2}) (Supporting Information, Figure S10). As the temperature increased, the CE dropped slightly because of accelerated crossover of vanadium ions, while the VE increased sharply because of the improved electrode kinetics and decreased ohmic polarization of the battery. An impressive battery performance with a CE > 98%, VE > 92%, and EE > 91% was observed even at a temperature as high as 50°C . Moreover, the battery ran continuously for 60 cycles at 50°C with no decay in efficiency (Supporting Information, Figure S11), and retention of capacity above 80%, further demonstrating the reliability and practicality of the zeolite-coated membrane. Considering the significantly low cost and excellent performance of this battery, the zeolite-coated membrane thus offers a promising alternative to Nafion in flow battery applications.

In summary, an effective approach for fabricating membranes with high ion selectivity using a simple PES based porous membrane coated with a shape selective zeolite flake was presented for the first time. The zeolite-coated membrane features a multidimensional channel network with an appropriate pore size and large numbers of exchangeable cations based at AlO_4^- sites, which are responsible for low vanadium permeability and high proton diffusivity. A VFB using the zeolite-coated membrane showed a CE of 98.63% and an EE of 91.41% at a current density of 80 mA cm^{-2} , which is much higher than a VFB using a pristine PES membrane under the same conditions. Moreover, the zeolite-coated membrane exhibited much higher battery efficiencies than a Nafion 115 membrane in response to current density, and a stable performance after more than 100 cycles in a charge–discharge test at a current density of 200 mA cm^{-2} . The low cost zeolite-coated membrane can thus be considered a promising sub-

stitute for high cost perfluorinated membranes, and will promote further research on zeolites and their applicability to ion-selective membranes.

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