



## Elimination of active species crossover in a room temperature, neutral pH, aqueous flow battery using a ceramic NaSICON membrane



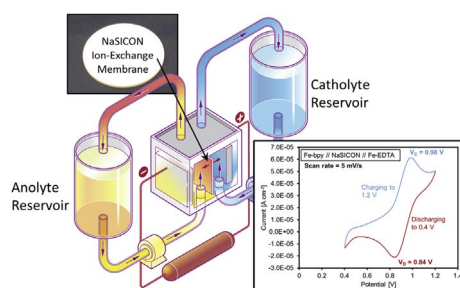
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### HIGHLIGHTS

- Active species crossover is a persistent challenge to flow battery energy storage.
- NaSICON ceramic demonstrates fast, stable Na-ion conductivity at room temperature.
- Aqueous flow battery chemistry effectively cycles using NaSICON as IEM.
- Use of NaSICON IEM is demonstrated to eliminate active species crossover.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Flow batteries are an attractive technology for energy storage of grid-scale renewables. However, performance issues related to ion-exchange membrane (IEM) fouling and crossover of species have limited the success of flow batteries. In this work we propose the use of the solid-state sodium-ion conductor NaSICON as an IEM to fully eliminate active species crossover in room temperature, aqueous, neutral pH flow batteries. We measure the room temperature conductivity of NaSICON at 2.83–4.67 mS cm<sup>-1</sup> and demonstrate stability of NaSICON in an aqueous electrolyte with conductivity values remaining near 2.5 mS cm<sup>-1</sup> after 66 days of exposure. Charge and discharge of a full H-cell battery as well as symmetric cycling in a flow battery configuration using NaSICON as an IEM in both cases demonstrates the capability of the solid-state IEM. Extensive analysis of aged cells through electrochemical impedance spectroscopy (EIS) and UV–vis spectroscopy show no contaminant species having crossed over the NaSICON membrane after 83 days of exposure, yielding an upper limit to the permeability of NaSICON of 4 × 10<sup>-10</sup> cm<sup>2</sup> min<sup>-1</sup>. The demonstration of NaSICON as an IEM enables a wide new range of chemistries for application to flow batteries that would previously be impeded by species crossover and associated degradation.

### 1. Introduction

The growth of renewable energy sources such as wind and solar has led to a need for large scale energy storage to accommodate the incorporation of these intermittent energy sources into the grid in a meaningful way. Flow batteries are an attractive and versatile technology to meet grid energy management needs due to their unique

capability to decouple power and energy considerations in design, their enhanced safety relative to other battery systems, and their extremely long cycle life that reduces the amortized cost of storage on such systems [1–4].

Flow batteries rely on active species that are in a liquid phase or are dissolved in a supporting liquid electrolyte, allowing storage of the active materials in external tanks where they can be pumped through

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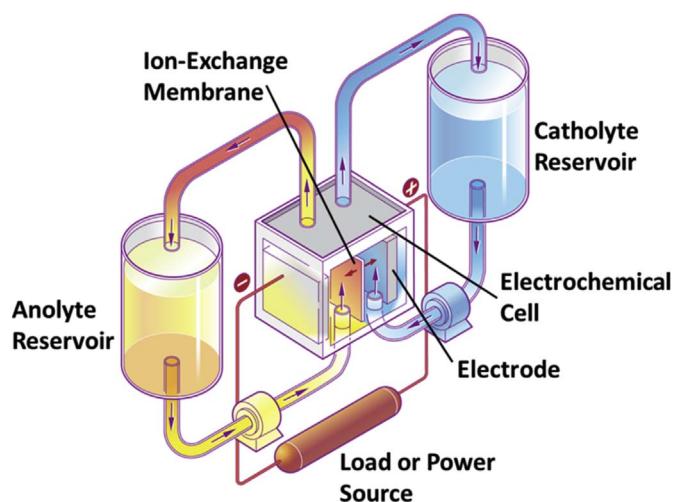


Fig. 1. Schematic of a traditional flow battery in which liquid catholyte and anolyte are pumped from external storage containers through the electrochemical conversion cell.

an electrochemical cell when desired for charge or discharge. A schematic for a typical flow battery setup is shown in Fig. 1. It's this external storage of active species that enables the decoupling of power delivery and energy storage capability of flow batteries, offering greater flexibility in system design and easy scalability to very large formats. These liquid-based active materials also mean that materials stresses and resulting degradation effects that build up over time and often shorten the life of solid state electrode materials are not present in flow battery active materials. As such, the theoretical cycle life of many flow batteries is extremely long [1–3]. The liquid anolyte and catholyte in flow batteries are composed of redox active species which, when pumped through the battery cell stack, can be oxidized or reduced to facilitate the charge or discharge of the battery. During discharge, for example, the redox-active anolyte species will be oxidized while the catholyte is reduced, with electron transfer occurring through the external circuit, delivering electrical power. To balance this transfer of electrical charge from the anolyte to the catholyte, a charge compensating ion will flow between the anolyte and catholyte through an ion-exchange membrane (IEM). This membrane must serve the dual role of selectively allowing transport of counter-ion across the cell interface while also physically separating the different redox active species of the catholyte and anolyte [5–7].

One of the biggest factors restricting the wide scale application of flow batteries – active species crossover – is heavily related to the IEM. Many investigated chemistries for flow batteries suffer from a deficiency in IEMs that can selectively allow for counter-ion flow without active species crossover [5–8]. When an active species crosses over the IEM, the contamination leads to both a loss of efficiency and a gradual degradation of the active solution with continued cycling, significantly shortening the effective battery life [5,8]. The iron-chromium system, for example, was one of the earliest developed and most heavily studied redox flow battery chemistries and though it paved the way for much future work in the field, iron-chromium technology never realized much success due to persistent issues with species crossover and membrane fouling [5,8,9]. The current state-of-the-art and most widely employed redox flow battery chemistry is the vanadium redox flow battery (VRB), which overcomes the species crossover issue by utilizing the same electroactive vanadium compound in both the catholyte and anolyte solutions [8,10,11]. This is enabled by the four stable oxidation states of vanadium, allowing for an anolyte of  $V^{2+}/3+$  and a catholyte of  $V^{4+}/5+$ . Whenever these active species crossover the IEM, which they inevitably do, it simply causes a reduction in the battery efficiency and state-of-charge balance issues but not degradation of the active material because it is chemically indistinguishable. Despite this

mitigation of the crossover issue, vanadium batteries still suffer from a number of issues that have limited their penetration into the commercial space after nearly 20 years of development [11]. Membrane crossover of the active species causes performance issues in the form of reduced coulombic efficiency and build up of charge imbalance between the positive and negative sides of the battery. This imbalance requires maintenance in the form of electrolyte re-balancing and if left unaddressed can result in a reduction of deliverable capacity from the cell and osmotic pressure difference across the IEM that can cause pumping issues or damage to the membrane [12–14]. In addition to these performance and maintenance issues, VRB's also suffer shortcomings through the use of toxic  $V_2O_5$  active material, corrosive sulfuric acid electrolytes, expensive functionalized IEMs, and expensive vanadium raw materials [5,6,10,15].

IEMs as currently employed in flow batteries are typically microporous polymer membranes with hydrophobic backbones for mechanical durability and hydrophilic side chains or termination groups that are functionalized to allow for selectivity in the charge and/or size of the species that can pass through them [5,7]. Functionalized IEMs can be either cation or anion exchange membranes to facilitate the flow of, respectively, positively charged or negatively charged ions. Most IEMs in flow batteries are cationic proton conductors that allow for the flow of small, positively charged  $H^+$  ions as the charge compensating ion. However, many active species are also positively charged and as such are more likely to penetrate cation conducting IEMs. One of the more widely employed polymer IEMs, and the one utilized in VRBs, is DuPont's commercially available Nafion. Nafion is a perfluorosulfonic acid polymer membrane composed of a Teflon backbone with sulfonic acid functional groups to allow for the transport of  $H^+$  ions. Nafion has several attractive qualities that have led to its widespread adoption, including high proton conductivity and chemical stability. However, it is also selectively permeable to water, suffers from high crossover contamination (diffusivity of  $V^{4+}$  measured at  $1.94 \times 10^{-4} \text{ cm}^2 \text{ min}^{-1}$ ), and is costly [5,16].

It seems imperative that in order to enable new flow battery chemistries other than vanadium, effort must be focused to eliminate the crossover of active species through the IEM in flow batteries. As such, we propose the use of the solid-state sodium super ionic conductor (NaSICON) as a zero crossover IEM for a room temperature, neutral pH, aqueous flow battery. With the use of a solid-state conductor as an IEM the method of ion conduction involves the solid IEM uptake of the counter ion, in this case  $Na^+$ , from solution into the solid conduction framework where it is transported across the membrane and then released into the solution on the other side. This is fundamentally different from the porous polymer mechanism of ion-conduction – which relies on liquid electrolyte for transport of the counter ion through membrane pores – and serves to realize the previously elusive goal of a crossover free IEM. The utilization of solid state conduction also isolates the solvent on each side of the flow battery such that different supporting electrolytes can be utilized for catholyte and anolyte solutions. This effective isolation is demonstrated in a study by Senthilkumar et al. in which two highly incompatible electrolytes in the form of metallic sodium and an aqueous catholyte are effectively separated and cycled using a NaSICON separator [17].

Among solid-state ion conductors NaSICON, with nominal formulation  $Na_3Zr_2Si_2PO_{12}$ , is uniquely suited for this application due to its very high room temperature conductivity and stability in a near-neutral water environment, both of which are also confirmed experimentally in this study [18,19]. A hybrid flow battery utilizing a solid state IEM of  $\beta''$  alumina was recently published in a system employing an aqueous catholyte [20]. In that case the solid-state conductor demonstrated an initial room temperature conductivity of  $\sim 1 \times 10^{-4} \text{ mS cm}^{-1}$ , which degraded severely under exposure to the aqueous catholyte to  $\sim 1 \times 10^{-6} \text{ mS cm}^{-1}$  after two months. Comparatively, our work here shows that NaSICON retains a conductivity of  $\sim 1 \times 10^{-3} \text{ mS cm}^{-1}$  after two months of aqueous electrolyte

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