



# Theoretical evaluation of electrochemical cell architectures using cation intercalation electrodes for desalination



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## ARTICLE INFO

### Article history:

Received 21 September 2016  
Received in revised form 30 January 2017  
Accepted 2 February 2017  
Available online 4 February 2017

### Keywords:

electrodialysis  
desalination  
intercalation  
Prussian Blue Analogue  
simulation  
flow

## ABSTRACT

Water scarcity is a dilemma facing much of the global population. Cation intercalation desalination (CID) cells, which use intercalation host compounds (IHCs) in combination with ion-exchange membranes (IEMs), could aid in addressing this challenge by treating saline water sources. Originally, the performance of such cells was predicted utilizing continuous flow of saline water through porous IHC electrodes. Here, we use two-dimensional porous-electrode theory with concentrated solution transport to evaluate the performance of various cell architectures where flow occurs through open flow channels (OFCs) when two IHC electrodes comprised of nickel hexacyanoferrate (NiHCF) are used to store  $\text{Na}^+$  ions. We show that, when two OFCs are used, cation exchange membranes (CEMs) are adjoined at flow-channel/electrode interfaces, and an anion exchange membrane (AEM) is arranged between flow channels, salt removal increases relative to the original design with flow-through (FT) electrodes. The IEM stacking sequence within such a membrane flow-by (MFB) cell is the fundamental repeat unit for electrodialysis (ED) stacks using many IEMs (CEM/AEM/.../CEM/AEM/CEM) with many diluate streams. Accordingly, we simulate the performance of such ED stacks using NiHCF IHCs, and we predict that salt adsorption capacity (per unit NiHCF mass) is amplified by twenty-fold relative to MFB and FT cells, while simultaneously decreasing 0.7 M NaCl feed water to 0.2–0.3 M within diluate streams. The generality of these findings is further supported by simulations using  $\text{Na}_{0.44}\text{MnO}_2$  IHC instead of NiHCF. Thus, we propose the use of cation IHCs as alternatives to the gas-evolution reactions used in conventional ED.

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## 1. Introduction

Recent analysis shows that the majority of the world's population experiences water scarcity for at least one month of the year [1]. Water reuse and desalination of salt-rich water sources (e.g., sea and brackish water) could reduce the burden of freshwater scarcity [2]. Pressure-driven reverse osmosis technology has substantial installed capacity around the world [2,3] but requires large-scale plants to desalinate water efficiently [4]. Alternative membrane technologies exist to desalinate water using electric potential as a driving force. Electrodialysis (ED) is the most developed of such technologies and has found extensive use in demineralization of salt-containing solutions [5]. In ED Faradaic reactions are used to induce electric potential drop across a stack of ion-exchange membranes (IEMs) with alternating selectivity toward cations and anions. When saline source water is pumped

through flow channels between IEMs their selectivity enables the generation of alternating streams of concentrated brine and desalted water, referred to as concentrate and diluate respectively [6]. Conventional ED stacks use gas-evolution reactions (e.g.,  $\text{H}_2$  and  $\text{O}_2$  gases [7]) to generate ionic current, and as a result costly metals [8] and large stacks are required.

Solid and solution-phase electrode processes offer benefits over the gas-evolution reactions used in conventional ED. Along these lines, reactions involving iron-based redox couples in solution, including hexacyanoferrates anions ( $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ ), have been evaluated for use in reverse ED [9–11], but their performance may be limited by crossover through IEMs due to their mobility in solution (as is commonly encountered in flow batteries using dissolved redox couples [12]). In contrast, capacitive deionization (CDI) uses the electric double-layers (EDLs) of high surface-area porous carbon to store cations and anions in solution [13]. CDI cells have also been developed with IEMs arranged on the surface of electrodes (MCDI), so as to minimize co-ion expulsion within EDLs [14]. Capacitive electrodes have also been incorporated into

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reverse ED to increase energy recovery from salinity gradients [15]. Other efforts in the CDI literature have been aimed at increasing salt removal, including through the use of flow electrodes [16] and a hybrid arrangement of Na-ion and capacitive electrodes [17,18]. Novel bi-porous carbons have also been employed to enable flow of electrolyte through the thickness of electrodes, rather than along the electrode's length [19].

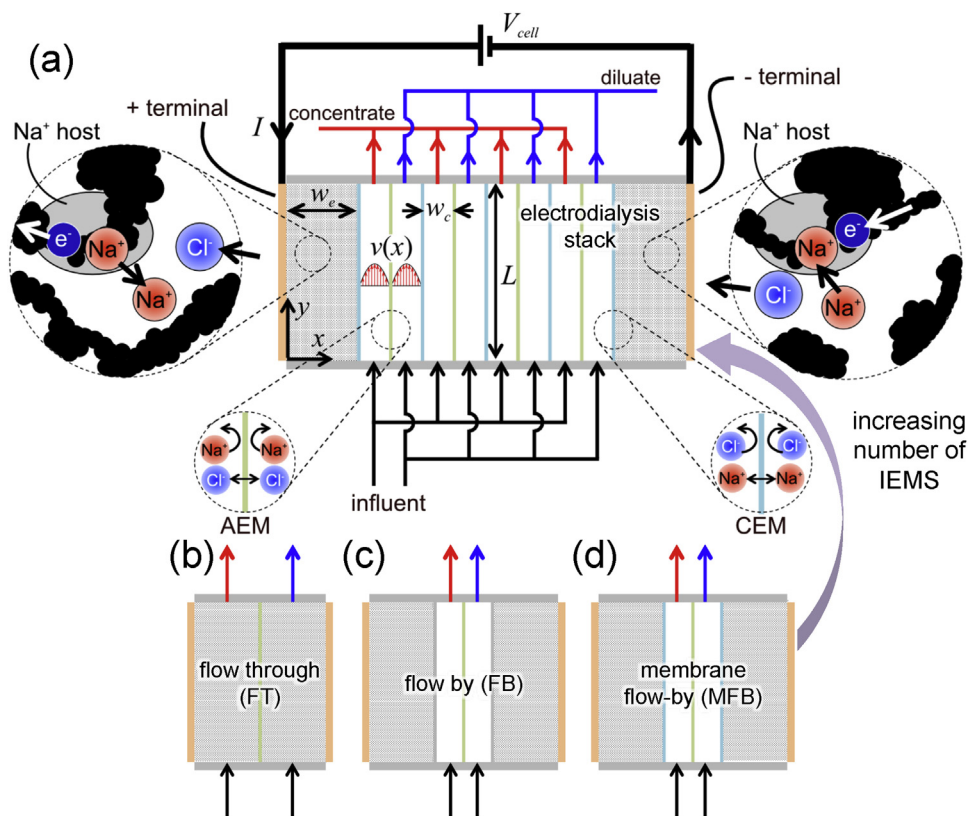
To enable desalination of seawater-level salt concentrations, other devices have employed solid-state Faradaic electrode reactions in lieu of capacitive electrodes. Specifically, the desalination battery used a Na-ion intercalation cathode paired with a Ag/AgCl conversion anode [20]. More recently, we predicted that a Na-ion battery containing intercalation electrodes can desalinate seawater-level salt concentrations if an anion exchange membrane (AEM) is used to suppress Na-ion transport between the electrodes [21,22].

This concept, which we refer to presently as cation intercalation desalination (CID), can be employed with generic intercalation host compounds. In our original work [21,22], we applied the CID concept with  $\text{Na}_{0.44}\text{MnO}_2$  (NMO) and  $\text{NaTi}_2(\text{PO}_4)_3$  (NTP), which exhibit sizable volumetric charge capacities (approximately 200 mAh/mL-NMO [23] and 400 mAh/mL-NTP [24]). Despite these advantages, the abuse tolerance of these materials may be limited due to the degradation of NMO as a result of over (dis)charge [25] and the propensity of NTP to hydrolyze in moderate pH solutions [24,26]. In contrast, the open framework structure of Prussian Blue Analogues (PBAs) has enabled facile intercalation and long cycle life in various aqueous cation batteries (including  $\text{Na}^+$  [27–30],  $\text{K}^+$  [27,28],  $\text{Ca}^{2+}$  [31], and  $\text{Zn}^{2+}$  [32] among other ions in general electrochemical cells [33]). While the components of Prussian Blue itself are soluble in aqueous solution when all Fe atoms therein have the same oxidation state (i.e., either all  $\text{Fe}^{\text{II}}$  or all  $\text{Fe}^{\text{III}}$ ) [33], its analogous structures formed by substitution of one Fe atom within

$\text{Fe}_2(\text{CN})_6$  with a different transition metal, including Ni [27], Cu [28], and Mn [34], are insoluble in aqueous and non-aqueous electrolytes. Thus, PBAs are metal hexacyanoferrate compounds, which use the same redox-active unit as hexacyanoferrate ionic complexes [9–11], but can be used as solid-state IHCs in aqueous electrolytes. Because of their open-framework structure, PBAs show substantially lower volumetric charge capacity than NMO and NTP (approximately 100 mAh/mL-PBA [27]). Aside from energy storage, nickel hexacyanoferrate (NiHCF) and copper hexacyanoferrate PBAs have recently been used to harvest energy from salinity gradients in aqueous NaCl solutions [35,36]. In addition, these materials can be synthesized in Na-rich [29,30] and Na-deficient [27,28] forms, enabling the construction of symmetric CID cells [21].

Theoretical and computational modeling is being employed increasingly to guide the development of electrochemical desalination devices, including in ED [37–46], capacitive deionization [14,19,47–51], CID [21,22], and other technologies [52–55]. Computational implementations of these models vary in dimensional fidelity, including zero- [39–42,49,51], one- [19,46], and two-dimensional models [21,22,37,38,43–45,48,55]. While capacitive [19,50,51] and Na-ion [21,22] models capture the local dynamics of charge adsorption, previous ED models have focused on accurate description of transport processes within flow channels and membranes [37–44], while neglecting the Faradaic reactions that draw current and induce electric field.

In this work we use a numerical model to predict the performance of cation intercalation desalination cells with various membrane and flow arrangements. We model nickel hexacyanoferrate as an intercalation host compound and show that, despite its low charge capacity, efficient desalination of seawater-level concentrations is possible in a range of CID device configurations. To perform these simulations we extend the fidelity of our two-



**Fig. 1.** (a) Schematic of a simulated electrodesalination stack utilizing Na-ion intercalation electrodes. Several other cells with only two flow channels were also simulated with Na-ion intercalation electrodes, including (b) a flow-through (FT) cell, (c) a flow-by (FB) cell, and (d) a membrane flow-by (MFB) cell.

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