A one-dimensional model for water desalination by flow-through electrode capacitive deionization

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HIGHLIGHTS

- A 1D improved modified Donnan model is developed for flow-through electrode cell architecture
- Suitable fitting parameters are obtained via fitting model to equilibrium charge and salt stored data from a custom-built cell.
- Model well-describes dynamic effluent salt concentration and cell current data, showing that flow-through CDI can be described with simpler 1D models.

ARTICLE INFO

ABSTRACT

Capacitive deionization (CDI) is a fast-emerging water desalination technology in which a small cell voltage of ~1 V across porous carbon electrodes removes salt from feedwaters via electrosorption. In flow-through electrode (FTE) CDI cell architecture, feedwater is pumped through macropores or laser perforated channels in porous electrodes, enabling highly compact cells with parallel flow and electric field, as well as rapid salt removal. We here present a one-dimensional model describing water desalination by FTE CDI based on modified Donnan electric double layer theory, and employing simple cell boundary conditions derived via scaling arguments. We further provide a comparison of model results to data obtained from a custom-built FTE CDI cell. We show good model-to-equilibrium data fits with reasonable values for fitting parameters such as the Stern layer capacitance, micropore volume, and attraction energy. Further, the model well-describes dynamic effluent salt concentration and cell current obtained from the experimental cell. Thus, we demonstrate that from an engineering modeling perspective, an FTE CDI cell can be described with simpler one-dimensional models, unlike more typical flow-between electrodes architecture where 2D models are required.

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1. Introduction

Capacitive deionization (CDI) is a rapidly growing research field, with primary applications in brackish water desalination and wastewater purification [1]. A CDI cell typically consists of two carbon-based porous electrodes that are electronically isolated by a separator, and feedwater is pumped through the cell. Applying a voltage across the electrodes causes charged ions in the feed to migrate to oppositely charged electrodes and to be electrostatically contained in electric double layers (EDLs) within micropores [2,3]. This process constitutes the charge half-cycle, and is also the desalination stage. Once the electrodes are fully charged, they can be discharged by short circuiting the electrodes, allowing the stored ions to be released into the flow and resulting in a waste brine stream. A number of CDI cell architectures have been developed [4–7], but the earliest and most common

architecture is composed of two electrodes separated by a separator channel, through which the feedwater is pumped. This architecture is often referred to as flow-by or flow-between electrodes (FB) [1].

An alternative CDI cell architecture is the flow-through electrode (FTE) architecture, where the feedwater flows directly through electrode macropores rather than between the electrodes (see Fig. 1a) [8–10]. One main advantage of FTE relative to FB is that the electric field and flow directions are parallel, allowing for facile optimization of ionic and flow resistances [8]. Further, since the separator is no longer the main flow channel in an FTE cell, the separator thickness may be minimized (provided the electronic isolation remains adequate), resulting in improved desalination rates and more compact cells [8, 11]. However, it has been reported that anode corrosion occurs at a faster rate in FTE CDI systems relative to FB systems, though nitrogen sparging to reduce dissolved oxygen content in the feedwater has been shown to increase FTE cell stability to a level comparable to FB cells [12]. Further, surface charge modification has been shown to reduce anode corrosion and improve charge efficiency in FTE systems

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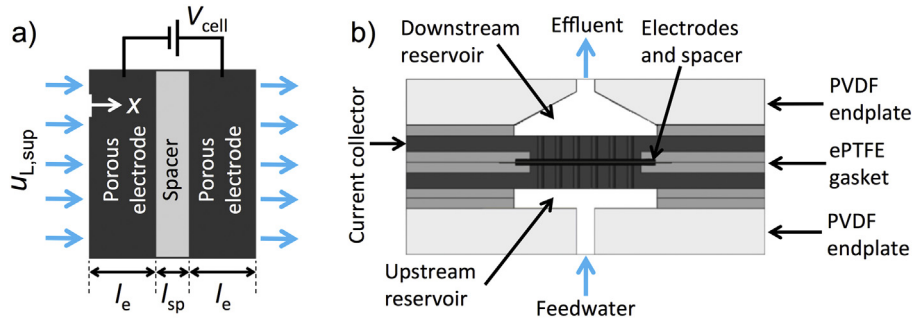 E-mail address: mesuss@technion.ac.il (M.E. Suss).

Fig. 1. a) Schematic of the 1D model domain, which includes both electrodes and the spacer. b) Schematic of the experimental FTE CDI cell used in this work, with cell dimensions provided in the Materials and methods section.

[9]. Another potential drawback of FTE is that such cells can require greater feed pressures than FB cells in order to flow through the electrodes' macropores with the desired throughput [8]. However, recent work by Guyes et al. has demonstrated that laser perforating electrodes with roughly 200 μm diameter flow channels enabled orders of magnitude improvement in electrode hydraulic permeability without affecting the electrodes salt adsorption capacity or gravimetric capacitance [13].

Several engineering models for water desalination by CDI have been proposed which couple macroscopic porous electrode theory to an EDL structure model [14–18]. The models developed to date are generally applied to flow-between CDI cells, where flow and electric field are perpendicular, necessitating a 2D model approach [17,18]. Hemmatifar et al. demonstrated the first fully 2D model for flow-between CDI cells, which employed a Donnan EDL model [18]. A widely-applied model utilizes a modified Donnan theory to describe the EDL in micropores of CDI electrodes, and which demonstrates good fits to data over a wide range of experimental conditions and electrode materials [19, 20]. While FTE CDI is a promising CDI cell architecture, to our knowledge there has not been a comparison between FTE CDI data to an appropriate model. We here develop a 1D model and simplified boundary conditions for FTE CDI cells, employing a modified Donnan EDL model. We further present the fitting of our model to FTE CDI data from a custom-built cell.

2. Theory

To develop a 1D FTE CDI model, we start with the volume-averaged, 1D, superficial molar flux of an ion, J_i, given by the extended Nernst-Planck equation,

$$J_i = c_{mA,i} \cdot \nu - D_{mA,i} \cdot \left(\frac{\partial c_{mA,i}}{\partial x} + z_i c_{mA,i} \frac{\partial \phi_{mA}}{\partial x} \right) \tag{1}$$

where $c_{mA,i}$ is the ion concentration in the macropores of the electrode (defined as a concentration per unit macropore volume), ν is the superficial fluid velocity of the electrolyte phase, $D_{mA,i}$ is an effective ion diffusion coefficient, z_i is the ion valence, ϕ_{mA} is the dimensionless macropore electric potential (which can be multiplied by the thermal voltage $V_T = RT/F$ to arrive at a dimensional voltage), and x is a spatial coordinate along the flow and electric field direction in our model FTE CDI cell (see Fig. 1a). The effective ion diffusion coefficient in the electrodes, $D_{mA,i} = p_{mA}D_{\infty,i}/\tau_{mA}$, where $D_{\infty,i}$ is the ion's molecular diffusivity, includes a correction for macropore porosity, p_{mA}, and tortuosity, τ_{mA}. For simplicity, we assume a binary electrolyte with univalent ions and equal cation and anion diffusivities, whereas future works will investigate the effect of more complex electrolyte solutions.

A conservation of species applied to anion or cation yields

$$\frac{\partial c_{eff,i}}{\partial t} = -\frac{\partial J_i}{\partial x} \quad , c_{eff,i} = p_{mA}c_{mA,i} + p_{mi}c_{mi,i} \tag{2}$$

where p_{mi} is the porosity of the electrode's micropores. We combine Eqs. (1) and (2) to arrive at salt and charge balance equations, given by

$$\frac{\partial c_{eff}}{\partial t} = -\nu \cdot \frac{\partial c_{mA}}{\partial x} + D_{mA} \cdot \frac{\partial^2 c_{mA}}{\partial x^2} \quad , \quad c_{eff} = p_{mA}c_{mA} + \frac{1}{2}p_{mi}c_{mi,ions}$$
$$p_{mi} \frac{\partial \sigma_{ionic}}{\partial t} = 2 \cdot D_{mA} \cdot \frac{\partial}{\partial x}\left(c_{mA}\frac{\partial \phi_{mA}}{\partial x} \right) \tag{3}$$

where c_{mA} is the macropore salt concentration ($= c_{mA,+} = c_{mA,-}$ by electroneutrality), $c_{mi,ions}$ is the total ion concentration in the micropores ($= c_{mi,+} + c_{mi,-}$), and σ_{ionic} is the ionic micropore charge ($= c_{mi,+} - c_{mi,-}$).

Micropores in porous CDI electrodes are responsible for salt electrosorption and present a highly confined geometry. One method for modeling the EDL structure within such confined geometry is a Donnan or modified Donnan approach [21]. In the Donnan approach, the potential in the micropore volume is assumed to be constant, independent of the distance to the carbon wall. Furthermore, assuming that ion transport between micropores and macropores (those at the same x-position) is rapid and so transport across the electrode thickness is rate limiting, Boltzmann's law relates ion concentrations in micro- and macropore volumes,

$$c_{mi,i} = c_{mA,i} \cdot \exp(-z_i \cdot \Delta\phi_D + \mu_{att}) \tag{4}$$

where $\Delta\phi_D$ is the (dimensionless) Donnan potential, defined as the potential within the volume of micropores relative to that in adjacent macropores. An empirical ion attraction term μ_{att} is used which aids in fitting of the theory to data (μ_{att} is assumed to be the same for both ions), which is an inverse function of total micropore ions concentration, $\mu_{att} = E/c_{ions,mi}$, with E a constant micropore attraction energy [22]. This approach has the advantage of relative mathematical simplicity and a good fit of data to theory [20,22]. More recent theories model the EDL structure without the use of a term μ_{att}, instead including charged surface groups in the micropores, termed an amphoteric Donnan model [23].

For the modified Donnan EDL model, mobile ionic charge in the micropores, σ_{ionic}, is equal in magnitude to the electronic charge, σ_{elec}, which resides in the carbon matrix surrounding the micropore, $\sigma_{ionic} + \sigma_{elec} = 0$. When anode and cathode have the same size and microporosity, the thickness-averaged electronic charge in one electrode is equal in magnitude to the average electronic charge in the other electrode: $\langle\sigma_{elec,A}\rangle + \langle\sigma_{elec,C}\rangle = 0$. In this case, we can relate the ionic current density in the separator layer, J_{ch}, to the averaged electrode