ELECTROCHEMICALLY MEDIATED DESALINATION

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ABSTRACT

Electrochemically mediated desalination (EMD) is an energy efficient and emerging method for membraneless seawater desalination. The technique separates ions from water as a result of oxidizing a small fraction of naturally abundant chloride ions, thus generating an ion depletion zone and locally elevated electric field gradient that increases ion electromigration. Here, we describe the operating principles of EMD, and demonstrate how applied potential bias, chloride concentration, flow rate, and electroactive surface area affect the desalination process.

KEYWORDS: Electrochemistry, Separation, Desalination, Electrophoresis, Water

INTRODUCTION

Fresh water is required to sustain life. However, the world is facing a global challenge to reliably supply its population with safe water due to shortages stemming from population growth,1 climate change,2 contamination of available fresh water supplies,3 and public policy.4 The available amount of water on Earth is relatively constant due to the hydrological cycle.5 However, supplies vary with time and location, therefore making localized water shortages commonplace. Only ~2.5% of water available on Earth is fresh water (<0.05% salts by weight).6 Of this amount, more than half is locked in glaciers and permanent ice, while remaining supplies are increasingly being contaminated with difficult-to-remove impurities.7 Importantly, ~97.5% of the world’s water supply is contained in easily accessible saline reservoirs, with ~1.0% being brackish groundwater (0.05-3.0% salts) and the remaining ~96.5% being seawater (3.0-5.0% salts). This suggests that the vast amounts of saline water could provide a nearly unlimited fresh water supply if coupled to an energy efficient desalination technology. Here, we present the operating principles of electrochemically mediated desalination (EMD),8 a membraneless desalination technique that our groups are currently developing.

EXPERIMENTAL

The EMD experiments reported here were carried out using either a PDMS/quartz or PDMS/glass hybrid microfluidic device outfitted with either a pyrolyzed photoresist carbon (PPC) electrode (82 μm wide) or Pt (100 μm wide) electrode, respectively. The Pt electrode was employed for all two-electrode experiments, while the PPC electrode was employed for all bipolar electrode (BPE) experiments. The procedure for assembling these devices is as follows. PPC or Pt microband electrodes were fabricated on quartz or glass substrates using AZ 1518 photoresist (AZ Electronic Materials, Somerville, NJ) and standard photolithographic techniques. The photoresist was spin coated onto the substrates at 500 rpm for 10 s, then 3500 rpm for 45 s, and finally 500 rpm for 5 s before being soft baked at 100 °C for 45 s. A mask aligner (Süss MicroTec, Garching, Germany) and photomask (CAD/Art Services, Inc., Brandon, OR) were used to achieve a desired electrode pattern on the substrate. The exposure was 10 s using a UV lamp intensity of 9.7 mW/cm². The substrates were then developed for approximately 12 s using AZ 400 K developer (AZ Electronic Materials) diluted 1/4 (v/v) with deionized water. The patterned photoresist substrates were then pyrolyzed in a quartz tube furnace (model 55035, Lindberg, Watertown, WI) with a forming gas of 5% H₂ and 95% N₂ (Regen, Praxair, Danbury, CT) continuously flowing at 100 sccm to yield the PPC electrodes. To prepare the Pt electrodes, electron beam deposition was used to deposit a 10 nm Ti adhesion layer followed by 100 nm of Pt onto the patterned photoresist substrate. Lift-off of the excess metal was performed in a sonicated acetone bath for 5 min.

PDMS microchannels (inlet: 2.5 mm long, 100 m wide, and 22 m tall, outlets: 2.5 mm long, 50 m wide, and 22 m tall) were fabricated from a single SU-8 2025 (MicroChem, Newton, MA) mold patterned on a silicon wafer (University Wafer, South Boston, MA). The brine outlet branched from the...
desalted stream at a 30° angle. Reservoirs were made using a 3 mm-diameter metal punch to remove PDMS at each microchannel extremity. The PDMS channels were rinsed with ethanol and dried under N₂ before both the PDMS and substrate were exposed to an air plasma (60 W, model PDC-32G, Harrick Scientific, Ossining, NY) for 15 s on the medium setting, and finally the two parts were bound together with the electrode aligned at the channel center and upstream of the Y-intersection (Figure 1). The microfluidic device was then placed in an oven at 65 °C for 5 min to promote irreversible bonding of the substrate and PDMS.

**RESULTS AND DISCUSSION**

To initiate desalination, a voltage is applied between the microfabricated Pt anode and wires present in the grounded reservoirs (Figure 1). This voltage is adjusted to a value that results in the oxidation of Cl⁻ (eq 1), which is present in seawater.

\[
2\text{Cl}^- - 2\text{e}^- \leftrightarrow \text{Cl}_2 \quad (1)
\]

This reaction reduces the number of ionic charge carriers (Cl⁻) present in the vicinity of the anode, thus giving rise to the depletion zone shown in red in Figure 1. Once the depletion zone forms, a disproportionate percentage of the applied voltage is dropped in this region, resulting in a locally elevated electric field. Note that both a BPE® or traditional two-electrode configuration can be used to generate this field, but here we focus on the more general and simplified two-electrode configuration illustrated in Figure 1.

The net velocity vector of ions present within the channel is determined by a summation of convection and electromigration. There is no net electroosmotic flow because it would be directed toward both the inlet and outlets from the channel center, but the absence of a fluid reservoir at the channel center precludes fluid flow. Convection, in the form of PDF, is created using a solution height differential between the inlet and outlet reservoirs. As shown in Figure 2, this results in a parabolic laminar flow profile that is uniform along the length of the channel. The local fluid velocity due to laminar flow is designated as \(u_l\), and this value varies across the width of the channel. The electrophoretic velocity \(u_{ep}\) of ions is governed by eq 2, where \(\mu_{ep}\) is the electrophoretic mobility, and \(V_l\) is the local electric field strength.

\[
u_{ep} = \mu_{ep} V_l \quad (2)
\]
Because the electric field strength is highest in the depletion region, \( u_{ep} \) will be greatest near the Y-intersection. In all regions of the channel in Figure 2, except near the depletion zone, ionic transport is dominated by PDF. Accordingly, the net movement of ions is toward the outlets. However, as ions approach the depletion zone and elevated \( V_t \), they experience an increasing \( u_{ep} \). At some point along the elevated \( V_t \), if the condition \(-u_{ep} > u_t\) is satisfied, the coupled transport between migration and convection causes cations to migrate away from the depletion zone and toward the brine stream, consequently producing desalted water. This situation is illustrated schematically by the vectors shown in Figure 2. To maintain electroneutrality within the microchannel, anions are also redirected into the brine stream.

The key to EMD is the elevated electric field strength resulting from Cl oxidation. To support this contention, the axial electric field profile was measured. When the microchannel is filled with seawater (red trace, Figure 3) or 0.50 M NaCl (blue trace, Figure 3), there is a sharp increase in the local electric field strength near the anode (centered at 2.5 mm) compared to when the channel is filled with 0.50 M \( \text{Na}_2\text{SO}_4 \) (black trace, Figure 3). This measurement supports the notion that Cl oxidation (eq 1) is key to EMD. Electric field strength measurements as a function of the applied potential bias, chloride concentration, flow rate, and electroactive surface area provide additional information about the operating principles of EMD.

Numerical simulations performed in 0.50 M NaCl solution with the assumption of Cl oxidation at the anode exhibit a local electric field gradient and a 20% reduction of salinity in the desalted stream. This result is in excellent agreement with experimental findings demonstrating salt rejection of 25 ± 5%. At a 50% recovery, the average flow rate of desalted water was approximately 0.04 \( \text{Lmin}^{-1} \), resulting in an energy efficiency of just 25 mWhL\(^{-1}\), near the theoretical minimum amount of energy required for this process (~17 mWhL\(^{-1}\)).

Accordingly, EMD compares favorably with efficient, state-of-the-art seawater desalination technologies.
desalination technologies, such as reverse osmosis, which typically operates at approximately 2000 mWhL⁻¹ (~99% salt rejection, 50% recovery) for a process that requires a theoretical minimum energy of approximately 1000 mWhL⁻¹.¹

**CONCLUSION**

In summary, we have established the basic operating principles of a membraneless and energy efficient technique for seawater desalination. EMD relies on the oxidation of Cl⁻, which generates an ion depletion zone and local electric field gradient to redirect sea salts into a brine stream. EMD provides a number of benefits relative to existing desalination technologies. First, the technique is membraneless, and therefore does not suffer from membrane fouling or damage, does not require high pressures for operation, and the source water does not require extensive pre-treatment prior to desalination. Second, EMD achieves energy efficiencies of 25 mWhL⁻¹ for 25 ± 5% salt rejection at a 50% recovery of desalted water (theoretical minimum is ~17 mWhL⁻¹). Lastly, the simple design, operation, and equipment required to perform EMD greatly reduces the capital costs associated with desalination. Our future work is focused on further understanding, optimization, and up-scaling of EMD.

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