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A comparison of multicomponent electrosorption in capacitive deionization and membrane capacitive deionization

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ABSTRACT

In this study, the desalination performance of Capacitive Deionization (CDI) and Membrane Capacitive Deionization (MCDI) was studied for a wide range of salt compositions. The comprehensive data collection for monovalent and divalent ions used in this work enabled us to understand better the competitive electrosorption of these ions both with and without ion-exchange membranes (IEMs). As expected, MCDI showed an enhanced salt adsorption and charge efficiency in comparison with CDI. However, the different electrosorption behavior of the former reveals that ion transport through the IEMs is a significant rate-controlling step in the desalination process. A sharper desorption peak is observed for divalent ions in MCDI, which can be attributed to a portion of these ions being temporarily stored within the IEMs, thus they are the first to leave the cell upon discharge. In addition to salt concentration, we monitored the pH of the effluent stream in CDI and MCDI and discuss the potential causes of these fluctuations. The dramatic pH change over one adsorption and desorption cycle in CDI (pH range of 3.5–10.5) can be problematic in a feed water containing components prone to scaling. The pH change, however, was much more limited in the case of MCDI for all salts.

1. Introduction

The shortage of fresh water has become a severe problem in our time owing to population and economic growth, as well as the impacts of climate change. This has made desalination of sea and brackish water stand out as an increasingly necessary answer to resolve the water crisis. Among desalination technologies, capacitive deionization (CDI) has attracted attention as an energy-efficient and promising electrochemical desalination technology, especially for low salinity brackish water (Bouhadana et al., 2010; Subramani and Jacangelo, 2015). In the most common approach to CDI, the influent stream passes between two high-capacitance electrodes made of porous carbon materials to which an electrical voltage or current is applied. As a result, anions and cations are temporarily stored on the porous surface of the oppositely charged electrode and a deionized stream with lower ion concentration flows out of the cell. Ion electrosorption is based on the formation of electrical double layers (EDLs) inside the micropores (<2 nm) of the electrodes (Porada et al., 2013). After a period of operation, the electrodes become saturated and require regeneration. In this step, the cell voltage or current is reduced to zero and adsorbed ions are released into a wastewater stream. To summarize, a CDI cycle consists of two steps, ion adsorption and ion desorption. While CDI is only economic for relatively dilute solutions, it has low energy consumption as it removes ions from the electrolyte rather than separating water from the salty stream, such as in reverse osmosis and distillation (Asquith et al., 2015; Liu et al., 2015).

To improve performance, ion-exchange membranes (IEMs) can be placed in front of the electrodes. This approach, which is one of the most recent developments in CDI, is called Membrane Capacitive Deionization (MCDI) (Biesheuvel and van der Wal, 2010). In this case, cation and anion exchange membranes placed in front of the negatively and positively charged electrodes, respectively, will only allow counter-ions to move from the bulk solution toward the electrode. By blocking almost all of co-ions, the desalination process is more efficient as there is less co-ion repulsion. Furthermore, the use of IEMs enables us to reverse the polarity of the cell during desorption, which leads to a more complete expulsion of counter-ions from the micro and macropores of the carbon (Zhao et al., 2012a). In addition to the favorable features of CDI including low

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energy consumption, easy regeneration and maintenance (Wang et al., 2015), MCDI operation is more stable which makes this technique an attractive water treatment technology for industrial applications (Kim et al., 2010). Biesheuvel et al. (2011), Zhao et al. (2012a) and Dykstra et al. (2016a) have presented comprehensive ion transport models for desalination using MCDI.

Ion charge and size plays an important role, given that the CDI process is based on temporary adsorption of ions inside the EDLs of the carbon micropores. However, few studies on CDI performance have focused on salts other than NaCl. Pioneers of this work were Gabelich et al. (2002) who investigated the sorption capacity of carbon aerogel electrodes for various monovalent and divalent ions. They reported that monovalents are preferentially removed over divalent ions due to smaller hydrated radii. Zhao et al. (2012b) similarly observed preferential adsorption of Na^+ over Ca^{2+}; however, they reported Na^+ replacement with Ca^{2+} later during adsorption. In contrast, Xu et al. (2008), Mossad et al. (2013) and Mossad and Zou, 2012) recognized ionic charge as the factor controlling the electrosorption preference in a competitive environment. It is worth mentioning that the last three research groups studied the CDI performance with an electrolyte consisting of non-equal concentration of ions. In other words, as the ion concentration is one of the variables influencing the removal rate of that specific ion, it is questionable to attribute the preferential electrosorption sequence reported by them to ionic charge alone. A few studies have investigated the effect of ion properties on electrosorption while keeping the concentration equal for different salts. Seo et al. (2010) reported selective ion removal for a mixture of cations including sodium, potassium, magnesium and calcium at different flow rates. They attributed the adsorption sequence to the pore size and structure of the carbon material. In another work, Huyskens et al. (2013) measured the ion removal for various monovalent and divalent salts; however, their result was not in agreement with that of Seo et al. (2010). Later, Han et al. (2014), in a comprehensive data collection on removal of various monovalent ions in CDI using different activated carbon cloths, showed that sorption capacity and competitive ion removal can be tuned by varying the accessible surface area of carbon and its micro to mesoporosity ratio. Discrepancies between these reports indicate that more research is needed to fully understand the competitive electrosorption of different ions, especially in the presence of divalent ions. In the area of EDL modelling, Suss (2017) extended the existing models by accounting for ion volume exclusion interactions to demonstrate selective ion removal based on ion size.

The focus in MCDI has predominantly been on the removal of different salts using novel electrodes or IEMs (Kim et al., 2016; Kim and Choi, 2012). However, very few research groups have compared the removal rate of different ions in MCDI using commercially available IEMs. In 2012, Kim et al. (2013) manipulated the removal of chloride and nitrate in single and mixed solutions by varying the current density in MCDI. In a recent publication, Tang et al. (2017b) studied the removal of sulfate in MCDI and observed more sulfate removal in a mixture of sulfate and chloride with equal molar concentrations. As diffusion of the ions through the IEMs occurs prior to ion adsorption inside the micropores, these are crucial in controlling the diffusion. To date, little effort has been made to compare the competitive removal of different cations and anions in CDI to that in MCDI at milliequivalent concentrations.

Another phenomena that is mostly overlooked in this area is the pH fluctuation over one adsorption/desorption cycle. Only recently have He et al. (2016) and Gao et al. (2017) addressed this issue over a range of CDI operating conditions. Tang et al. (2017a) probed into details of pH fluctuation in batch mode operation of CDI and MCDI by monitoring the concentration of H_2O_2 and dissolved oxygen, and measuring the electrode potentials. Yet, we believe this phenomenon requires more research especially for a wide range of monovalent and divalent salts.

In this work, we aim to investigate the role of ion affinity to both the carbon electrode and the ion exchange membrane. To cover a wide range of ionic properties, experiments are conducted with NaCl, KCl, $CaCl_2$, $NaNO_3$, and Na_2SO_4 for single and mixed electrolyte solutions in both CDI and MCDI cells. To better understand the competitive electrosorption process, experiments were conducted at milliequivalent concentrations.

2. Materials and methods

2.1. Materials

In this work, we utilized the analytical grade of all chemicals. Activated carbon (AC Norit SA 4, Cabot Norit Activated Carbon, USA), polyvinylidene fluoride (PVDF, Mw ~530,000, Sigma-Aldrich), N–N dimethylformamide (DMF, 99.8%, Merck Millipore) and graphite sheet (DSN 530, Suzhou Dasen Electronics Material Co., China) were utilized for electrode fabrication. Sodium chloride (NaCl, 99.7%), potassium chloride (KCl, 99%), calcium chloride ($CaCl_2$, 99%), sodium nitrate ($NaNO_3$, 99%) and sodium sulfate (Na_2SO_4, 99%) were used to prepare electrolyte solutions. Solutions were prepared using water purified with a Millipore RIOs Large with a resistance of 1 MΩ cm.

2.2. (M)CDI setup and electrosorption experiment

Preparation of carbon electrodes using AC Norit SA4 as the carbon source, PVDF as the binder and DMF as the solvent is explained in detail in our previous work (Hassanvand et al., 2017). Electrodes of 10 cm by 20 cm with a narrow channel of 0.3 cm by 8 cm were fabricated using graphite sheet as the current collector. The carbon content was limited to 6.5 ± 0.5 mg cm^{-2} and the apparent thickness of the electrode materials cast on the current collector was 150 ± 15 μm obtained from SEM images. The prepared electrodes were then characterized using a surface and pore analyzer and cyclic voltammetry. The BET surface area was calculated as 540 ± 4 m^2 g^{-1}, and pore size distribution was indicative of a microporous structure with pore diameters ranging from 0.7 to 1.5 nm. For more details see our previous work (Hassanvand et al., 2017).

The CDI cell consists of two parallel AC electrodes sheets with a 0.9 mm gap which is filled by a non-conductive spacer (Low Foulant spacer 34 mil, Sterlitech). Anion and cation-exchange membranes (Neosepta AMX, thickness of 170 μm, and Neosepta CMX, thickness of 140 μm) are placed in front of the carbon electrodes, to configure the MCDI cell. All layers in the stack are compressed into a poly(carbonate) housing. A DC power module (N6731B, Agilent) in a modular power system mainframe (N6700B, Agilent) was used as the power source and electrical voltage and current across the cell was recorded at a rate of 1 reading per second.

Adsorption was conducted at a constant electrical voltage of 1.5 V while desorption followed at zero voltage in CDI and a reversed polarity of −1.5 V in MCDI. In the single-pass mode of operation, the feed solution passed through the cell at a flow rate of 20 ml min^{-1} using a peristaltic pump (NEMA 4X, Watson Marlow) and conductivity and pH (S470-kit, Mettler Toledo) of the effluent was monitored. Conductivity data are converted to salt concentration using the calibration curve corresponding to each salt. Salt adsorption (Q) in ($\mathrm{mmol_{salt}\ g_{carbon}^{-1}}$) can be calculated as below: