MEMBRANE CAPACITIVE DEIONIZATION

Albert van der Wal and Hank Reinhoudt
Voltea b.v., Wassenaarzegeweg 72, 2333 AL, Leiden, the Netherlands
Presenter Hank Reinhoudt
Corresponding author: Hank.Reinhoudt@voltea.com

Keywords: Desalination, ion removal, brackish water, ion exchange membranes

1 Introduction and background

Capacitive Deionization (CDI) is an electrochemical desalination technology which is suitable for the removal of ions from brackish water up to concentrations of about 8000 ppm. In CDI ions are removed from feed water by applying an electrical potential difference between two electrodes, which are separated from each other by a spacer compartment. Water can flow in the spacer compartment between the oppositely charged electrodes and the ions that are removed from the feed water are temporarily stored in the electrical double layers that are formed at the electrode-water interface.

The electrodes need to be regenerated once they are saturated with ions, which can be done by reducing or even reversing the applied voltage. After the ions have been released from the electrodes they can be flushed out of the spacer compartment, resulting in a waste stream concentrated in ions. After regeneration of the electrodes the system is again ready to remove ions from the feed water. The electrodes are often made from carbonaceous material such as activated carbon or carbon aerogel, which are electrically conductive and at the same time have a high storage capacity for ions due to the large internal specific surface area, of the order of $10^3 \text{ m}^2/\text{gr}$.

A comprehensive review of CDI technology is given by Anderson et al. (ref 1) and a theoretical model is presented by Biesheuvel et al. (ref 2).

![Figure 1: Schematic representation of two MCDI cells, showing the location of the ion exchange membranes as well as the direction of the water flow.](image)
In 2001 Andelman and Walker (ref 3) developed a Membrane based Capacitive Deionization (MCDI) technology, which significantly improved the efficiency of ion removal during desalination and ion release during electrode regeneration. In a typical MCDI set-up anion and cation exchange membranes are placed in front of the anode and the cathode, respectively, as can be seen in figure 1. In the same figure the direction of the water flow through the spacer compartment is also indicated, which is normally from the outside to the inside. In MCDI systems it is common to use current collectors, which are connected to the power source and which facilitate the transport of electrical charge in and out of the electrode.

In the current paper we discuss experimental results of MCDI operation which show how MCDI is ideally suited to achieve both high ion removal efficiency and high water recovery, which makes this an attractive technology for many applications.

2 Material and Methods

Experimental data were obtained using a MCDI stack which consisted of 13 repeating cells, with each square cell having a surface area of 36 cm\(^2\). The electrodes used were PACMM™ 203 (ex Material Methods) and the anion and cation exchange membranes were purchased from Tokuyama Co. (Neosepta AM1 and CM1). The spacers were purchased from Sefax and had a thickness of 110 µm and the current collectors were made from graphite. The MCDI stack was placed in a housing as shown in figure 2. The feed solution consisted of a 500 ppm NaCl solution, which was desalinated for 150 s at 1.5 V at a flow rate of 50 ml per minute, followed by a regeneration for 30 s at -1.5 V without flow (the concentration step) and 30 s at -1.5 V at a flow rate of 50 ml per minute (the waste step).

Figure 2: Picture of the housing containing 13 repeating MCDI cells, which was used for the desalination of water containing 500 ppm NaCl.
3 Results and Discussion

In figure 3 we present the desalination and regeneration results for several cycles of MCDI. We observe how in the MCDI technology which incorporates ion exchange membranes, more than 95% salt removal can be obtained. It is important to note that the water recovery, which is the ratio between the amount of purified and feed water, is very high, about 86% in this case.

![Desalination and regeneration cycles for MCDI](image)

Figure 3: Desalination and regeneration cycles for MCDI. This set of 11 cycles shows the high repeatability of the MCDI process.

The effect of the ion exchange membranes on the desalination efficiency in MCDI can be explained as follows. During the charging of the electrodes (desalination step), counterions are incorporated in the electrical double layers that form at the internal surface areas in the porous electrodes, whereas at the same time co-ions are expelled from the electrical double layers. The expelled cations from the anode electrode and the expelled anions from the cathode electrode recombine in the spacer or flow compartment, hence effectively reducing the salt removal efficiency.

At very low cell potentials or very high salt concentrations, the uptake of counterions and the exclusion of co-ions is exactly balanced and effectively no salt is removed from the feed water. At higher cell potentials and/or lower salt concentrations relatively more counterions are incorporated in the double layer. In MCDI the same process occurs, i.e. counterions are incorporated in the electrical double layer and the co-ions are expelled. Nevertheless, the expelled
co-ions cannot enter the flow channel due to the fact that they are blocked by the presence of the anion and cation exchange membranes. Because of charge neutrality these co-ions need to be compensation for by counterions, which can pass the ion exchange membrane and which can only come from the spacer or flow compartment. In an ideal MCDI process the electronic charge is therefore exactly charge balanced by counterion adsorption, which means that the transfer of one electron from the anode to the cathode electrode is accompanied by the removal of exactly one salt molecule out of the feed water stream. In theory, the charge efficiency, which is the ratio of the ionic charge over the electrical charge is therefore unity in case of MCDI. This is in agreement with observations made in a previous paper (ref 4) where we have presented a theoretical process model for the time dependent ion flux through the ion exchange membrane during desalination as well as ion release from the electrodes during regeneration. On the other hand, Zhao et al (ref 5) have shown that for CDI the charge efficiency can be significantly below 1, especially at lower cell potentials and/or higher salt concentrations in the feed water.

The ion exchange membranes in MCDI not only increase the efficiency of ion removal, but also play an important role in the regeneration of the electrodes. During the concentration and waste steps at reversed polarity ions are released from the electrode. In CDI, these ions will first enter the spacer compartment, but might subsequently migrate to the opposite electrode, where they will again be stored in the electrical double layer at reversed polarity. Therefore, in CDI a significant part of the ions are being transported between the two opposite electrodes and a relatively small fraction of the ions are removed from the waste stream.

Instead, in MCDI, the counterions that are released from the electrode during the concentration and waste steps cannot migrate to the opposite electrode, because the released anions from the anode cannot pass the cation exchange membrane and the released cations from the cathode cannot pass the anion exchange membrane. Therefore, in MCDI, high concentrations of neutral salt are obtained in the flow compartment during the concentration step, which can subsequently be flushed out during the waste step with low volumes of water, resulting in a high water recovery.
4 Conclusions and Applications

MCDI is a versatile new technology that offers significant benefits over existing CDI technology. The use of ion exchange membranes in front of the electrodes improves the ion removal efficiency and at the same time allows high water recoveries. The fact that the charge efficiency approaches unity in case of MCDI implies that the electrical charge can be very effectively used for the removal of salt from feed water, which results in reduced energy cost and opens up the potential of energy recovery. In addition, the ion exchange membranes reduce the fouling of the electrodes through scaling because they prevent the precipitation of hardness ions in the electrodes.

It is foreseen that MCDI will be used for a range of applications, which include industrial applications such as salt removal in cooling towers and groundwater desalination as well as mass market applications such as water softening devices in consumer households.

References