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Long term stability of capacitive de-ionization processes for water desalination: The challenge of positive electrodes corrosion

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ABSTRACT

Corrosion of the positive electrodes, in capacitive deionization (CDI) cells for water desalination processes, is a major problem that may prevent them from becoming practically important. This paper deals with the consequence of the corrosion of the positive electrodes in CDI processes on the desalination performance, in terms of capacity and the ratio between adsorption of counter-ions and desorption of co-ions. The detrimental effect of the positive electrodes oxidation on the de-ionization efficiency is demonstrated and discussed. The role of the potential difference applied to CDI cells on the electrodes' stability was explored as well. We used for this study CDI cells comprising several pairs of activated carbon electrodes and 3 electrodes cells containing reference electrode. The interrelated parameters measured included potential, current, concentration (translated from conductivity measurements) and pH vs. time. The present study and the understanding gained herein, will enable the development of durable, long term and effective CDI processes.

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1. Introduction

Due to the increasing need for potable water, the search for energy-efficient water purification is widespread, with the most widely investigated methods being electrodialysis [1–3], electro-static shielding [4–6] and ion exchange [7–9]. The most frequently examined and used methods for water desalination are reverse osmosis [7,10,11] (RO) and direct distillation (DD) [12], which require extensive amounts of energy either for maintaining high pressure (RO), or to evaporate water from the saline mixture and condensate it (DD).

Capacitive deionization (CDI) is an energy-efficient water desalination method for brackish water (BW) that contains 500–5000 ppm of salt [13]. In this method, the solution flows through cells comprising sets of two high-surface area electrodes which are periodically charged by applying constant potential differences between the electrodes. Thus, the salt is extracted from the saline water in a capacitive way, so part of the charge consumed during the electrodes' charging can be exploited back upon discharge of the cell. The electrodes used in CDI are usually carbonaceous materials with high surface area of hundreds of m^2/g, e.g., activated carbon fibers (ACF) and carbon aerogel [14–16]. In our work we use ACF electrodes. Activated carbon electrodes in CDI cells are expected to undergo very prolonged charge/discharge

cycling, because the process mainly involves electrostatic, non-chemical interactions [17,18].

Desalination of water by CDI can be operated in two modes related to the flow of solution in the cell: 'flow-by' [19–33], in which the solution flows in parallel to, between the electrodes and 'flow-through' [34–41], in which the solution flows in perpendicular to, through the electrodes. Using the flow-through regime, the solution has to flow through macro-porous electrodes. Their porous structure has to allow a smooth flow of solution through them. A very suitable electrodes' material for 'flow through' CDI cells is carbon cloth comprising activated carbon fibers.

Our previous work [39] showed a very interesting phenomenon occurring during prolong CDI processes in 'flow through' cells (repeated charge–discharge cycling), which was referred to therein as the "inversion effect". In the experiments described therein [39], the changes in solution concentration upon periodic operation of the CDI cells were monitored by continuous (on line) ionic conductivity measurements at the outlet of the cell. When the cell is polarized, electro-adsorption and hence removal of salt (reflected by low conductivity) are expected, while shortening the cell should result in an increase in salt concentration (discharge) and hence an increase in ionic conductivity. The "inversion effect" was reflected by desorption of ions (a rise in conductivity) while the cell was being polarized and charged. In turn, ions were depleted from the solution (decrease in conductivity) when the cell was discharged. The "inversion effect" was indirectly attributed to the continuous corrosion of the positively polarized electrodes, during charging.

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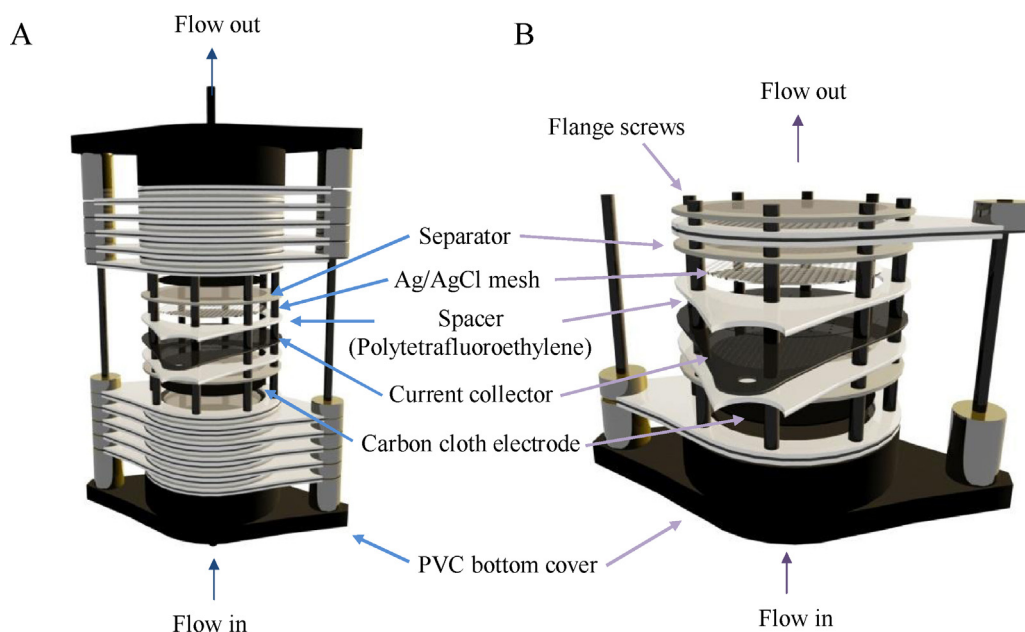
Fig. 1. (A and B) Schemes of the flow-through cells used in this work. All the components are explained in the figures and in Section 2.1.

Another effect that should be taken under consideration, and that can contribute to the "inversion effect" is the prevention of the complete desorption of the adsorbed ions due to the complex pores structure of the activated carbon electrodes. Thus as the electrodes are polarized, after the potential is removed, there are remaining counter-ions trapped in pores, which charge can hold some co-ions [20].

The work described in this paper was devoted to understand the "inversion effect", how it depends on the parameters of the CDI process, especially the applied potential. Corrosion inhibition of the positive electrodes in capacitive deionization (CDI) processes can help to make them an effective water desalination technology. Several long term experiments with different cells were conducted in order to understand what happens to CDI cells during prolonged operation. The impact of the applied potential was explored. The use of chemically oxidized electrodes in these processes was examined as well. Possible corrosion processes of the carbon electrodes were investigated. The parameters measured included potential, current, salt concentration at the exit of the cells and the extent of salt removal (translated from conductivity measurements) and changes in pH of the solution that flows through the electrodes. The present study is highly important, because the understanding gained herein, can help to promote CDI further as a promising method for desalination of brackish water.

2. Experimental

2.1. The CDI Cells structure

The CDI cell was designed for the "flow-through" mode, as described in Fig. 1. The cell has a flange-type design. The solution is introduced through plates in order to ensure homogeneous flow of the solution through the whole circular cross section of the cell. The electrodes were discs (54 mm wide, 0.5 mm thick) made of commercial carbon cloth (ACC-5092-15) from Nippon Kynol, Japan, possessing high surface area (1440 m^2/g BET) originating from phenol–formaldehyde polymeric fibers that underwent carbonization and activation. The CDI cell, shown in Fig. 1A contains 20 pairs of ACF disk electrodes (positive and negative); the CDI stuck contains 10 cells and each cell contains 2 pairs of ACF electrodes.

Sheets of porous polypropylene cloth served as separators between the electrodes and exhibited a fairly low resistance to the solution flow. Silicon glue was soaked into the rims (at the perimeters) of the separator discs, thus forming soft and elastic gaskets. These separator sheets with the gaskets at their perimeters provided the necessary mechanical and electrical separation between the electrodes (thus preventing short circuits). The cases for the electrodes were ring spacers, made of poly-tetra-fluoro-ethylene (PTFE), possessing 0.5 mm deep grooves that hold the carbon electrodes. The current collectors are made of graphite paper discs (Grafoil Inc.) that are attached to the electrodes in the cell. These graphite sheets current collectors are perforated to allow a smooth flow of solution through them. When all these components: electrodes in their plastic cases, graphite sheet current collectors, separator sheets with polymeric gaskets at their perimeter are pressed together, in the right order, they form hermetically sealed 'flow through' multi electrodes electrochemical cell. We used such cells containing a reference electrode (RE). The RE was Ag mesh covered by AgCl (by anodization of the silver mesh in NaCl solution) which was placed at the middle of the cell (Fig. 1A). This RE could be also used as auxiliary electrode. The content of its AgCl layer was calculated [34] to be equivalent to more than 3 times the charge that can be stored in the electrical double layer of the electrodes in the cell (assuming 1 V was applied between the electrodes). A simpler cell which included three-electrode cell containing two sheets of ACF electrodes as the working electrode (WE) and two Ag/AgCl electrodes as the counter and reference electrodes, was also used (Fig. 1B). All the CDI experiments were carried out using the cell described in Fig. 1A except for one experiment indicated by Fig. 11, which was carried out using the cell described in Fig. 1B.

2.2. The system set-up

A graphical explanation of the layout of the entire setup used herein, is presented by Fig. 2. A 20 l round-bottom flask was used as the solution reservoir for the experimental system. It contained 18 l of 1000 ppm of NaCl (>99% pure, Frutarom, Israel) solution in highly purified water (18.2 MΩ) that was circulated in a closed system which included the electrochemical cell, the pumps and the various detectors. Two conductometers (Metrohm, 712 model) were