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To cite this version:

Kelsey B. Hatzell, Etsuro Iwama, Anaïs Ferris, Barbara Daffos, Koki Urita, et al.. Capacitive deionization concept based on suspension electrodes without ion exchange membranes. Electrochemistry Communications, 2014, 43, pp.18-21. 10.1016/j.elecom.2014.03.003 . hal-01917272

HAL Id: hal-01917272

https://hal.science/hal-01917272v1

Submitted on 9 Nov 2018

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Official URL: https://doi.org/10.1016/j.elecom.2014.03.003

To cite this version:

Hatzell, Kelsey B. and Iwama, Etsuro and Ferris, Anaïs and Daffos, Barbara and Urita, Koki and Tzedakis, Théo and Chauvet, Fabien and Taberna, Pierre-Louis and Gogotsi, Yury and Simon, Patrice *Capacitive deionization concept based on suspension electrodes without ion exchange membranes.* (2014) Electrochemistry Communications, 43. 18-21. ISSN 1388-2481

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Short communication

Capacitive deionization concept based on suspension electrodes without ion exchange membranes

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ARTICLE INFO

Keywords:
Capacitive deionization
Capacitive suspension electrodes
Water desalination
Electrochemical flow capacitor
Flowable electrodes

ABSTRACT

A new type of capacitive deionization (CDI) system, based on capacitive suspension electrodes (CSEs), was developed for the purpose of desalting brackish and seawater through the use of flowable carbon suspensions. CSEs derived from activated carbon and acetylene black demonstrated a specific capacitance of 92 F g^{-1} in a static mode in a 0.6 M NaCl solution. The novel system introduced here is a proof of concept that capacitive suspension electrodes can be envisioned to desalt water without the aid of ion exchange membranes (IEMs).

1. Introduction

Creating access to safe and clean drinking water has emerged as one of the greatest research challenges across the globe [1,2]. With projected upcoming water shortages, researchers are looking toward non-traditional water sources, brackish and seawater, as a means to augment the water supply. This trend toward desalination is already apparent in countries like Qatar and the United Arab Emirates where 100% of the potable water is derived from the desalination of seawater [3,4].

The currently available desalination technologies include multi-effect distillation (MED), thermal-based multi-stage flash (MSF), and reverse osmosis (RO) techniques [5]. Among these techniques, RO is the current state of the art because it requires less energy than traditional thermal-based methods [1]. Nevertheless, RO plants require large capital investments, and become more cost effective on larger scales. There is a need for new innovative, flexible and sustainable technologies for water desalination to address the growing broader needs for clean drinking water.

Among the proposed new technologies, capacitive deionization has reemerged as a technological option for desalting brackish and, eventually, seawater [6]. Due to parallel developments in both the manufacturing and synthesis processes of nanostructured carbon materials, CDI technologies have gained additional attention [7–10]. However, poor scalability due to current system designs which rely on cyclically charging and discharging the cell, has limited CDI to small-scale systems and stifled widespread implementation. Recently, the flow capacitor concept has been demonstrated for grid energy storage [11–13], and in membrane capacitive deionization systems [14]. This approach eliminates many parts of conventional supercapacitor cells [15] and offers a pathway to large systems and lowering the cost of electrical energy storage. Herein, we introduce a new CDI technology based entirely on ion removal by flowable carbon suspensions without ion exchange membranes (IEMs). Flowable capacitive suspension electrodes (CSEs) address three key challenges currently impeding the scale-up and implementation of CDI technologies. These challenges include the ability to separate concentrated and clean water streams [9,16], the benefit of having a controlled and constant concentration at the outlet of the charging cell [17,18], and the opportunity for energy recovery (if coupled with an electrochemical flow capacitor [11]). Herein, we demonstrate the desalination of water via the use of CSEs without IEMs.

2. Concept

In a traditional CDI system, an applied voltage between two parallel carbon electrodes produces adsorption of ions in an electric double layer

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http://doi.org/10.1016/j.elecom.2014.03.003

(Fig. 1A). The concentration at the effluent is thus decreased until the electrode ion storage capacity is reached, after which deionization cannot occur without an ion release step (Fig. 1B). In contrast, in CDI based on CSEs (Fig. 1C), the carbon is constantly replenished in the channel, and thus a constant concentration occurs at the effluent (Fig. 1B).

A flowable electrode can be made by mixing sea or brackish water with an active material (activated carbon) to create a flowable slurry, herein called a suspension-type electrode. Two suspension-type electrodes flow through polarized plates, where the carbon adsorbs the salt ions as counterions into the electric double layer. At the end of the channel, the carbon and water can be sieved to produce lower concentrated solution (Fig. 1C). This sieving process only requires the use of simple low-cost porous separators (i.e. polymeric or non-woven glass fibers). It is envisioned that after sieving, the carbon can be flushed in a high concentration stream, discharged, and recycled for further use.

3. Materials and methods

3.1. Suspension preparation and material characterization

The suspension electrodes were prepared by mixing an anisometric activated carbon (AC) powder CECA AB [19] (LACQ CECA Arkema Group, 1800 m^2/g), with a conductive additive (acetylene black [AB], 65 m^2/g) and an electrolyte solution. The weight ratio of AC:AB was 3:2 and an aqueous electrolyte (0.6 M NaCl) was then added to achieve 14 wt.% (solid-to-liquid ratio). Another active carbon material, MAST spherical activated carbon (Carbon International Ltd, UK, 1345 m^2/g), was studied for comparison.

3.2. Electrochemical and system performance

As a proof of concept, the suspension performance was studied in static with volumetrically balanced electrodes. Cyclic voltammetry (CV) was carried out at 1 mV s^{-1} sweep rate. From the CV, the specific gravimetric capacitance (C_{sp}) was calculated by integrating the current versus potential plot using Eq. (1).

$$C_{sp} = \frac{2}{\Delta E} \cdot \frac{\int idV}{v \cdot m} \tag{1}$$

where ΔE is the voltage window, i is the discharge current, V is the voltage, v is the sweep rate, and m is the mass of activated carbon in one electrode. The factor of two accounts for the two symmetrical electrode setups. Electrochemical impedance spectroscopy (EIS) was used to measure the ohmic resistance of the cell, R_Ω (intersection with the real axis). All spectra were run in the frequency range of 200 kHz to 10 mHz at a sine wave signal amplitude of +/− 10 mV.

In order to address the desalination performance (adsorption capacity) of the capacitive suspension electrodes, a potentiometric titration measurement (using $AgNO_3$) was carried out on the suspension electrodes after undergoing chronoamperometry for 4.5 h at a potential of 0.5 V in order to evaluate the chloride ion adsorption efficiency.

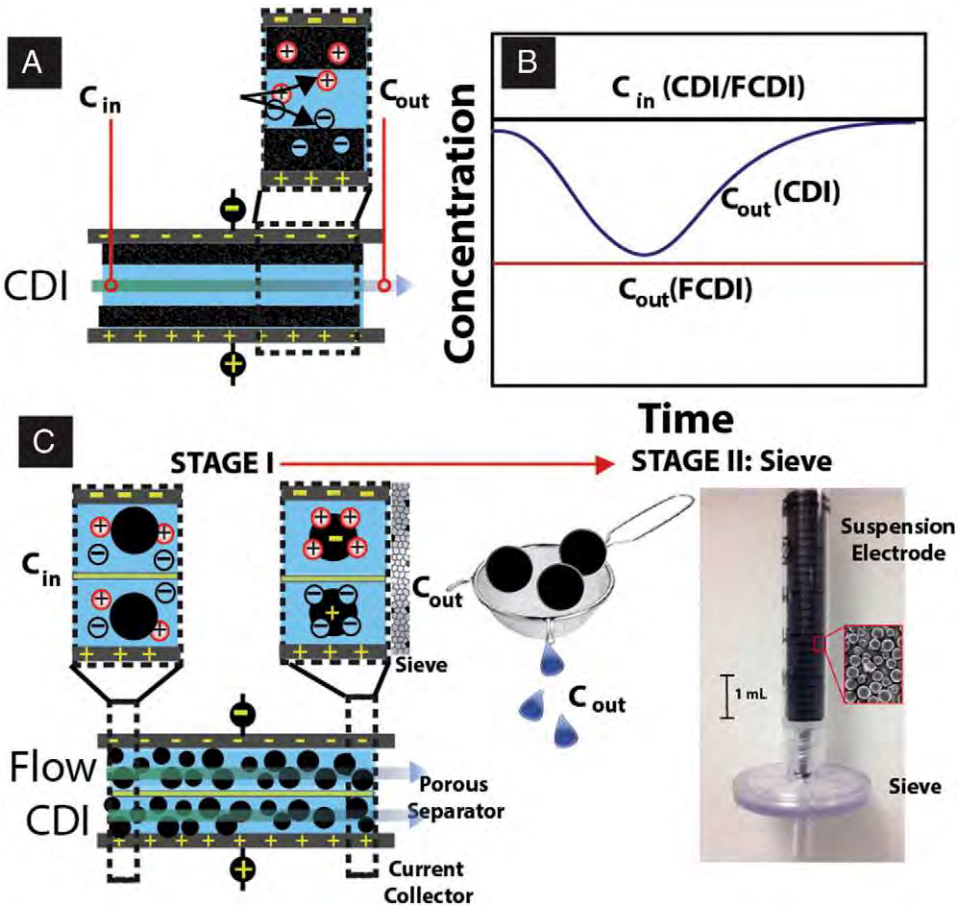

Fig. 1. A traditional CDI system with film electrodes (A) demonstrates a transient effluent concentration because of adsorption capacity limitations in film electrodes (B). In CDI based on CSEs, sea or brackish water can be combined with carbon to form a flowable electrode (C) and, when flowed between polarizing plates the carbon can adsorb the ions in the electric double layer. Carbon with adsorbed ions can then be separated to produce clean water through a sieving process and recycled. The sieve process to obtain clean water does not need membranes, but instead just a filter where the size of the pores is greater than the size of the carbon particles (~100 μm) (B).

4. Results and discussion

The electrochemical performance of the suspension electrode was assessed in a static configuration: a half-cell was assembled, and then the silicone rubber gasket was filled with a suspension [(CECA (3):(2) AB) 1:6 NaCl (0.6 M)]. A separator was placed across the gasket, and another gasket was placed on top. The second compartment was subsequently filled, and then the cell was closed and electrochemically characterized with cyclic voltammetry (CV). The cell was then compressed with screws in a uniform manner, such that the flowable electrode made good contact with the current collector, and sedimentation was not an issue during testing. Fig. 2A is a representative CV of a suspension electrode which led to a gravimetric capacitance (for 1 mV s^{-1}) of ~92 F g^{-1}. The suspension electrode was also characterized with EIS. Fig. 2B shows an ohmic resistance (R_Ω) of ~1.6 Ω which is respectable based on the ohmic resistance reported in similar suspension electrode systems [12].

For assessing desalination ability of such suspension, the system was held at 0.5 V for 4.5 h leading to a current decaying to approximately ~3.5% of the initial current (stationary leakage current). The cell was then disassembled, and the catholyte, where anions are adsorbed, extracted. A theoretical approximation (100% efficiency) of the chloride ions adsorbed was determined by integrating the current over the 4.5 h of the potentiostatic step. A total charge of Q = 10.3 A·s was found, which leads to an total amount of adsorbed ions (Na^+/Cl^-) of 0.11 mmol.

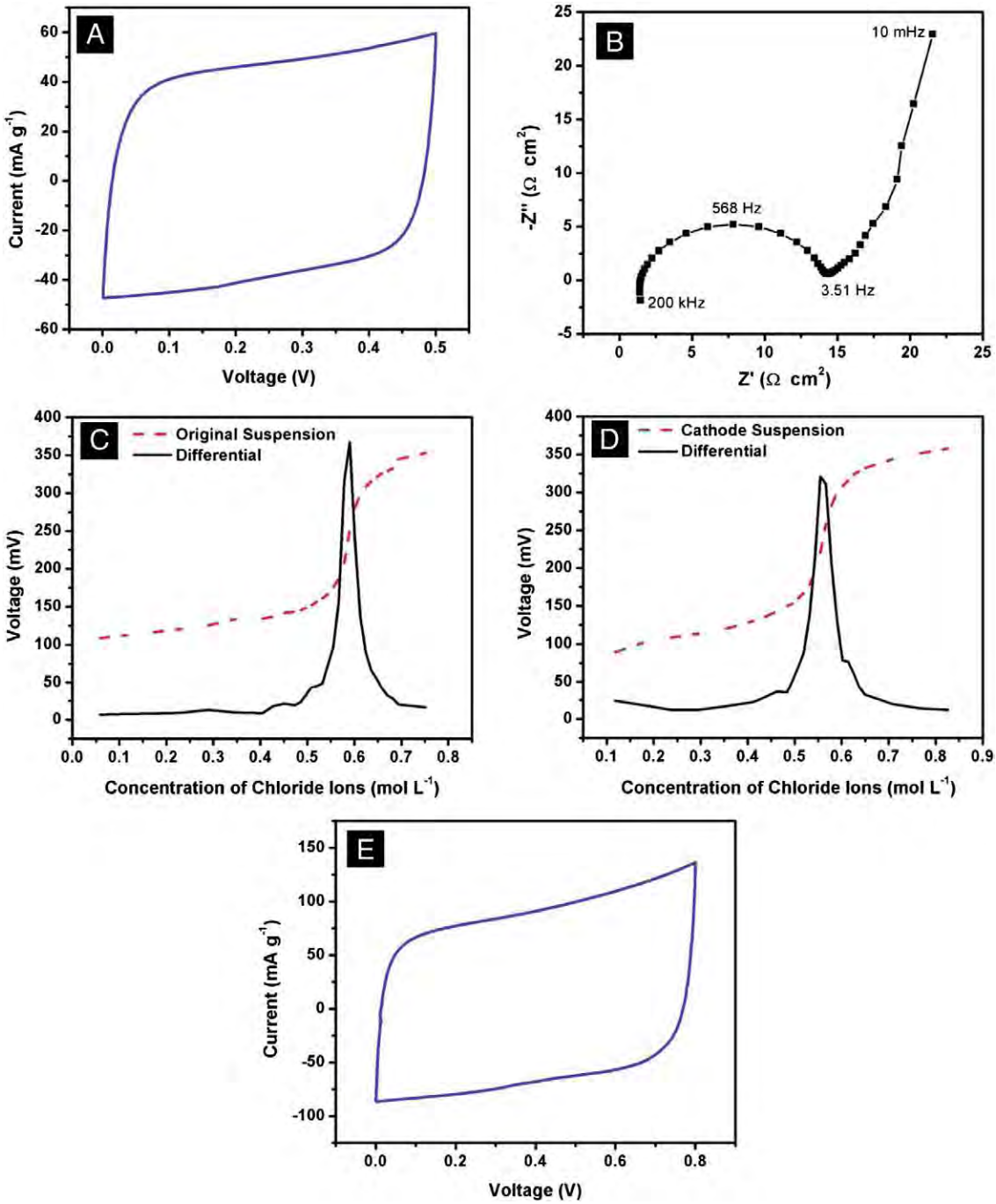

Fig. 2. Cyclic voltammetry (1 mV s^{-1}) of flow cell is in a static mode (A), the EIS of the static cell (B), and titration curves before (C) and after polarization (D). CV (1 mV s^{-1}) of 22.5 wt.% MAST carbon suspension electrode [MAST(9):(1) AB] 1:3 NaCl (0.6 M). Details on suspension electrodes derived from MAST activated carbon spheres can be seen in references [13,12] (E).

The concentration of ions adsorbed in the suspension was determined by comparing a suspension electrode with the suspension after polarization through a titration process with $AgNO_3$ (0.03 mol/L) [20]. Fig. 2C shows a titration of the suspension before undergoing polarization exhibiting a sharp peak after 5.20 ± 0.1 mL of $AgNO_3$ is added to the suspension electrode which leads to 0.59 mol/L concentration. Whereas Fig. 2D shows a titration of a suspension electrode after polarization leading to a chloride concentration of 0.55 mol/L. Using Eq. (2), we determined that the overall adsorption efficiency was ~68%. η is the amount of ions adsorbed (removed) per unit charge injected into the cell [21,22].

$$\eta = \left[\frac{F\Delta Cl^{-}_{titration}}{Q} \times V\right] * 100 \quad (2)$$

where $\Delta Cl^{-}_{titration}$ is the experimental concentration of ions adsorbed in the suspension, Q is the amount of electrical charge (in Coulombs) added to the cell, V is the cell volume, and F is Faraday's constant.

The titration results also revealed that during one charging period, 0.04 mol/L of ions is removed through adsorption. These results demonstrate the feasibility of the approach and we believe that the efficiency of the suspension electrodes can be greatly enhanced through cell design, and suspension optimization. Furthermore, we operate our system at 0.5 V, and we expect that charge efficiency will improve at higher voltages [23]. The use of spherical activated carbon particles, as shown in Fig. 2E, allows a much higher carbon loading, up to 23–27%, improving conductivity and capacitance of the slurry, but still maintaining the required flow properties [11–13]. Fig. 2E shows the cyclic voltammetry in static mode of a suspension containing 22.5 wt.% of MAST activated carbon leading to a capacitance of 150 F g^{-1}. Recently, Biswal et al. reported the synthesis of an activated carbon obtained from dead neem leaves exhibiting a very high capacitance of 400 F g^{-1} in aqueous electrolyte [24]. A 25-wt.% suspension-type electrodes made of this type of carbon, could theoretically transform seawater into drinkable water in one charging period. Thus, the desalination efficiency of this process can be greatly enhanced through material development, and is an open area for examination.

In this proof-of-concept study we demonstrate a new, potentially low-cost and scalable capacitive deionization system based on flowable carbon electrodes. The performance and desalination efficiency of flowable carbon electrodes were assessed electrochemically. In a static mode, a gravimetric capacitance of ~92 F g^{-1} and ~68% adsorption efficiency were achieved. This promising result, suggests that with cell design and material optimization, this concept may yield a high electrosorption capacity system capable of meeting and exceeding performance of traditional CDI systems.

Conflict of interest

There is no conflict of interest.

Acknowledgments

K.B.H. was supported by the NSF Graduate Research Fellowship (Grant # 1002809). E.I. and P.S. acknowledge the support from the European Research Council (ERC, Advanced Grant, ERC-2011-AdG, Project 291543-IONACES). A.F. was supported by the Erasmus Mundus programme (Materials for Energy Storage and Conersion program) from the European Commission. K.U. acknowledges the support from the Japan Society for Promotion of Science (JSPS, Strategic Young Researcher Overseas Visits Program for Accelerating Brain Circulation, R2307). The authors would like to thank the Partner University Fund (PUF) for funding the collaborative effort between Paul Sabatier and Drexel Universities.

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