Final project report

Sustainable graphene-based nanocomposites for water desalination using capacitive deionization technology (project 19-725)

I.   Summary of results

Accessing freshwater, one of the most fundamental human needs, has become more and more challenging during the past decades. The continuous growth of population and energy consumption is, together with alarming climate changes, expected to have an increasingly negative impact on the life conditions on Earth. Currently, more than one billion people around the world are suffering from a shortage of clean water and its adverse consequences on health, food and energy.

A key technology that could mitigate this trend is the development of cheap, long-term stable and effective systems for combined seawater desalination and ion purification. In this project, we have developed disruptive electrochemical cells for seawater desalination and ion purification. The main obtained results can be summarized as:

- Implementation of a novel porous carbon paper (C-paper) matrix for fabrication of capacitive deionization (CDI) electrodes.
- Successful seeding of the carbon matrix fibers by a homogenous ultrathin conformal layer of zinc oxide nanoparticles (ZnO-NPs) using a novel sol-gel technique.
- Realized CDI electrodes by growing zinc oxide nanorods (ZnO-NRs) on the seeded carbon matrix fibers.
- In-depth characterization of the nanocomposite CDI electrodes using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).
- Fabricated supercapacitor with CDI electrodes with confirmed capacitive behavior.
- Electrochemical characterization of the CDI electrodes using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronopotentiometry (CP), and chronoamperometry (CA) measurements.
- Demonstrated excellent stability of the CDI electrodes after 500 desalination cycles.
- Extracted desalination performance of the CDI electrodes.
- Finalized journal article presenting this work.

II.   Background

Among all existing desalination techniques, e.g., reverse osmosis and thermal distillation, capacitive deionization (CDI) is a promising energy-efficient and cost-effective approach for water desalination. The CDI technology is membrane-free, and it operates at low voltages based on the principle of an electrical double-layer capacitor. An external voltage is applied to a set of porous capacitor electrodes with saline seawater flowing through the capacitor (see Fig. 1). Saline sea water contains sodium chloride (NaCl) dissociated into salt ions i.e., Na^+ (cations) and Cl^- (anions). These anions and cations are separately electro-adsorbed on the porous electrodes due to the electric field generated by the external voltage. The adsorbed salt ions subsequently diffuse into the interior of the electrodes, where they accumulate in the porosities, forming an electric double-layer capacitor. When the layer pores are saturated with salt ions, a reverse voltage will be applied to desorb the ions and regenerate the electrodes.
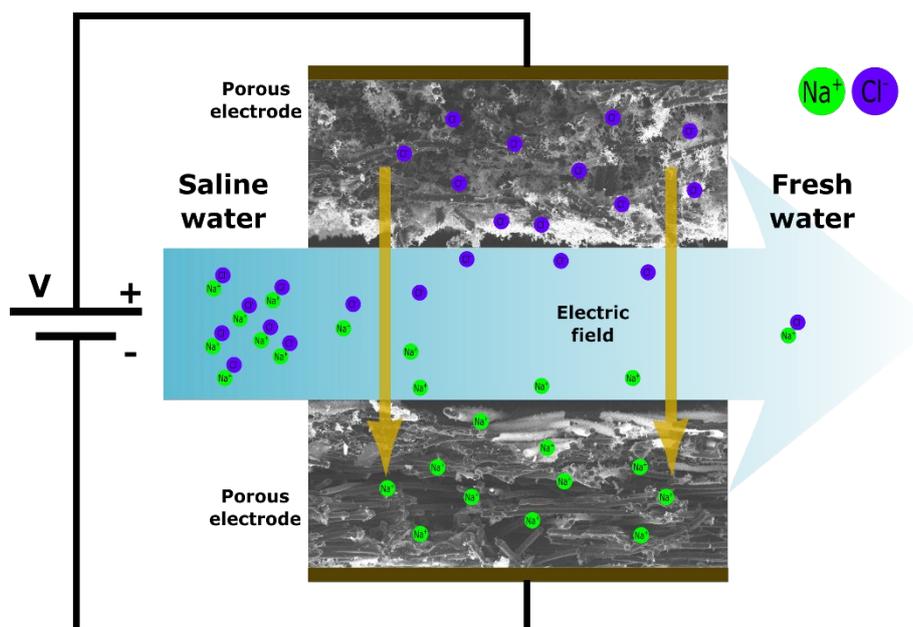
Fig. 1. Schematics of a CDI setup

III.   Results and Discussion

In this project, we have focused on the investigation of carbon/zinc oxide (ZnO) nanocomposites for water desalination: phase 1) synthesis, characterization, and realization of suitable carbon/ZnO composites, and phase 2) investigation of the desalination performance of optimized carbon/ZnO composite electrodes. In the first phase, the two available carbon materials, graphene, and carbon fibers were investigated with respect to the required properties for implementation as efficient desalination electrodes. The typical requirements of such electrodes include a high conductivity, a high mechanical and chemical stability, a large surface area, and excellent compatibility with hydrothermal growth of ZnO nanostructures. Although both proposed carbon materials showed excellent conductivity and stability properties with a solid attachment to the grown ZnO nanostructures, a special carbon paper (C-paper) with a dense carbon fiber network was selected as our final candidate. It provides a larger active surface area, a maximum porosity, and a thicker stable substrate for developing stand-alone CDI electrodes.

ZnO nanorods were grown on C-paper with strong bonding and mechanical stability by inexpensive low-temperature (<100 C) hydrothermal solution-based procedures. ZnO is a well-known unintentionally electron-rich (n-type) metal oxide (semiconductor with a wide direct bandgap). The nanorods were also doped with aluminum (ZnO:Al) to tune their conductivity for further increased desalination efficiency.

In order to optimize the properties of the present nanocomposite CDI electrodes, we improved the wettability (i.e., the hydrophilicity) of the carbon fiber papers by precoating them with a novel thin uniform layer of ZnO-NPs by a sol-gel method, followed by an annealing step at 300 ˚C. Fig. 2 below shows the SEM images of bare C-paper (left image), revealing its intricate dense carbon fiber network, and (b) individual carbon fiber coated with ZnO-NPs (right image). The homogeneity of the conformal layer of ZnO-NPs is readily observed in this high-resolution SEM image. Subsequently, ZnO-NRs were grown on the seeded C-paper by cost-effective, low-temperature chemical bath deposition. The final nanocomposite structure is

shown in Fig. 3. Energy dispersive x-ray spectroscopy (EDS) spectra (Fig. 4) show the uniform distribution of the different chemical elements in a cross section of the C-paper.
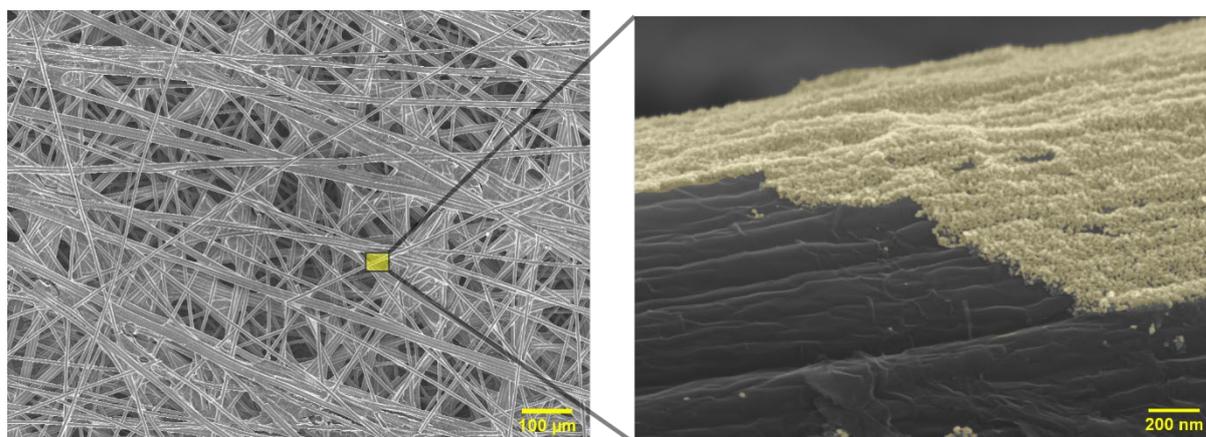

Fig. 2. SEM image of bare C-paper (left image). Carbon paper coated with ZnO-NPs (yellowish layer, right image).
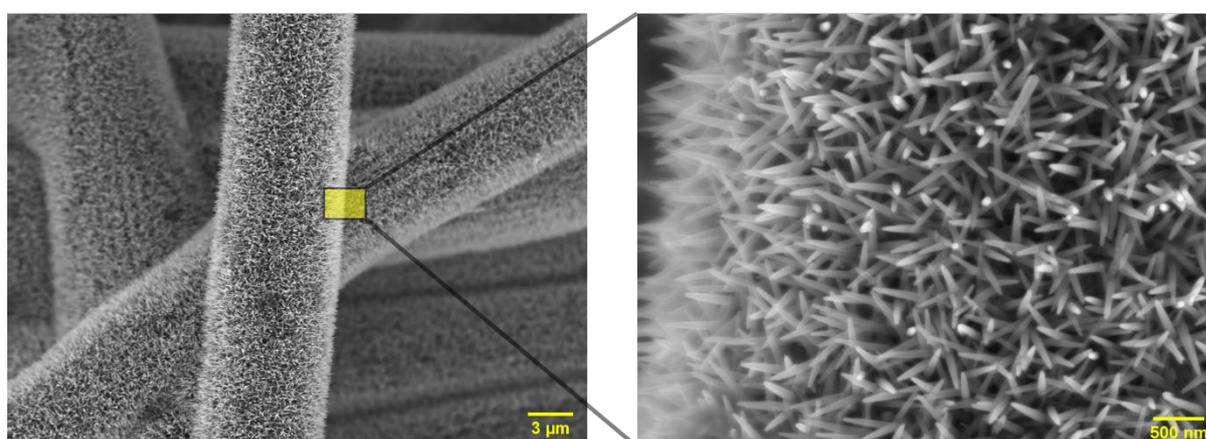

Fig. 3. SEM image of ZnO-NRs grown on C-paper coated with ZnO NPs (Fig. 2).

In the second phase of the project, the desalination performance of the developed electrodes was investigated with various electrochemical techniques. All measurements were carried out at room temperature using a three-electrode system with a 1 cm^2 area comprising an Ag/AgCl reference electrode and a platinum counter electrode in a 20 mM NaCl aqueous electrolyte (representing the saline seawater). To assess the desalination efficiency, we have fabricated four different types of prototype supercapacitors consisting of i) bare C-paper, ii) C-paper with ZnO-NPs (C-ZnO(NPs)), iii) C-paper with ZnO-NPs and ZnO-NRs (C-ZnO) and iv) C-paper with ZnO-NPs and ZnO-NRs doped with Al (C-ZnO:Al). Immersing the electrodes into the electrolyte forms an electric double layer at the interface which will act as an ion storage when an external voltage is applied. Here it is critical that no charge transfer occurs through the interface (no faradaic redox reactions are allowed). Faradaic reactions usually lead to an irreversible formation of undesirable by-products, so-called electrode poisoning, which seriously degrades the CDI cell stability. The cyclic voltammetry (CV) sweep in Fig. 5(a) shows faradaic reactions for negative voltages and non-faradaic, or equivalently a capacitive behavior, in the positive voltage range. This indicates that the C-ZnO electrodes can only be used in the positive voltage range without degrading.
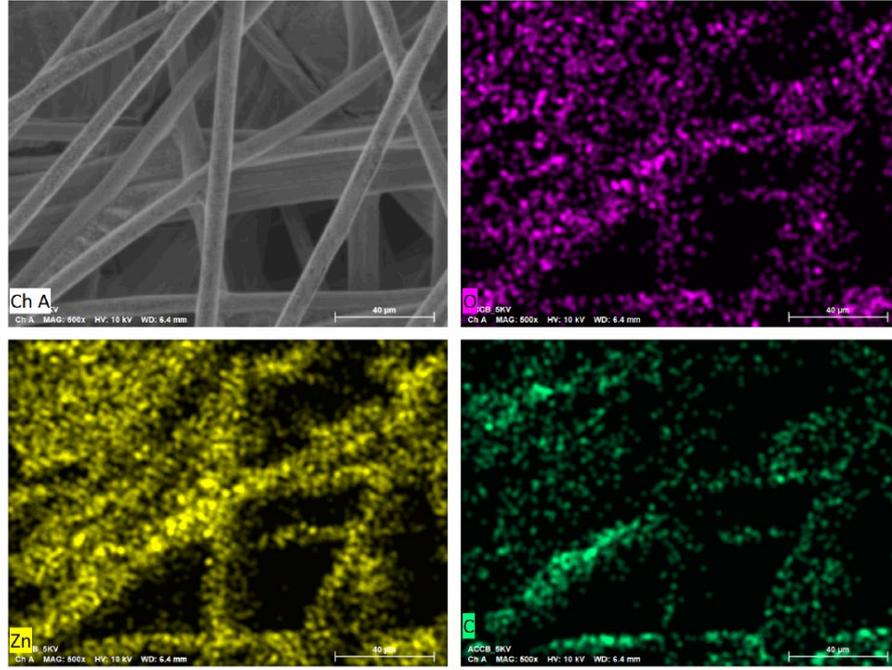
Fig. 4. SEM image of carbon fibers after growth of ZnO-NRs (upper left). The corresponding distributions of the different elements on the fibers in the same area are shown in the other three images: oxygen (upper right), zinc (lower left), and carbon (lower right).

Cyclic voltammetry measurements at various scan rates (Fig. 5(b)) confirm the excellent capacitor-like behavior of the best CDI supercapacitor nanocomposite electrodes made of C-paper decorated with ZnO. The differential capacitance, C_{diff}, of the electrochemical double-layer capacitor is given by the relation:

$$C_{diff} = \frac{\partial Q}{\partial V} = \frac{I}{dV/dt} \Rightarrow C(F/cm^2) = \frac{J}{v}$$

Here Q is the charge, V is the voltage and v is the bias scan rate (Volt/s). By plotting the extracted current density J from Fig. 5(b) versus scan rate and fitting the data to straight lines, as shown in Fig. 5(c), the voltage dependence of C_{diff} can be extracted (Fig. 5(d)). The desalination efficiency is directly proportional to this capacitance. Figure 5(d) shows the capacitance of all four tested CDI electrodes at different biases. Our results show a very promising increase in capacitance, from 19 $\mu F/cm^2$ for the bare C-paper to 1.2 mF/cm^2 for the nanocomposite C-ZnO electrodes (SEM images in Fig. 3 & 4).

In addition, chronopotentiometry (CP, or equivalently galvanostatic charge/discharge) measurement results presented in Fig. 6(a) show a conventional triangular-shaped charge/discharge cycling behavior. Both CV and CP results prove the capacitive storage mechanism of C-ZnO electrodes in NaCl electrolytes. The capacitance of the electrodes decreases with increasing current density passing through the desalination cell, as shown in Fig. 6(b).

The stability of the C-ZnO electrode was furthermore investigated by charging and discharging the electrode at a current density of 200 $\mu A.cm^{-2}$ for 500 desalination cycles. Figure 6(c) shows a less than 10% reduction in the capacitance of the C-ZnO electrodes after completing the cyclic test. This important result confirms the excellent stability of the C-ZnO electrodes for water desalination applications.
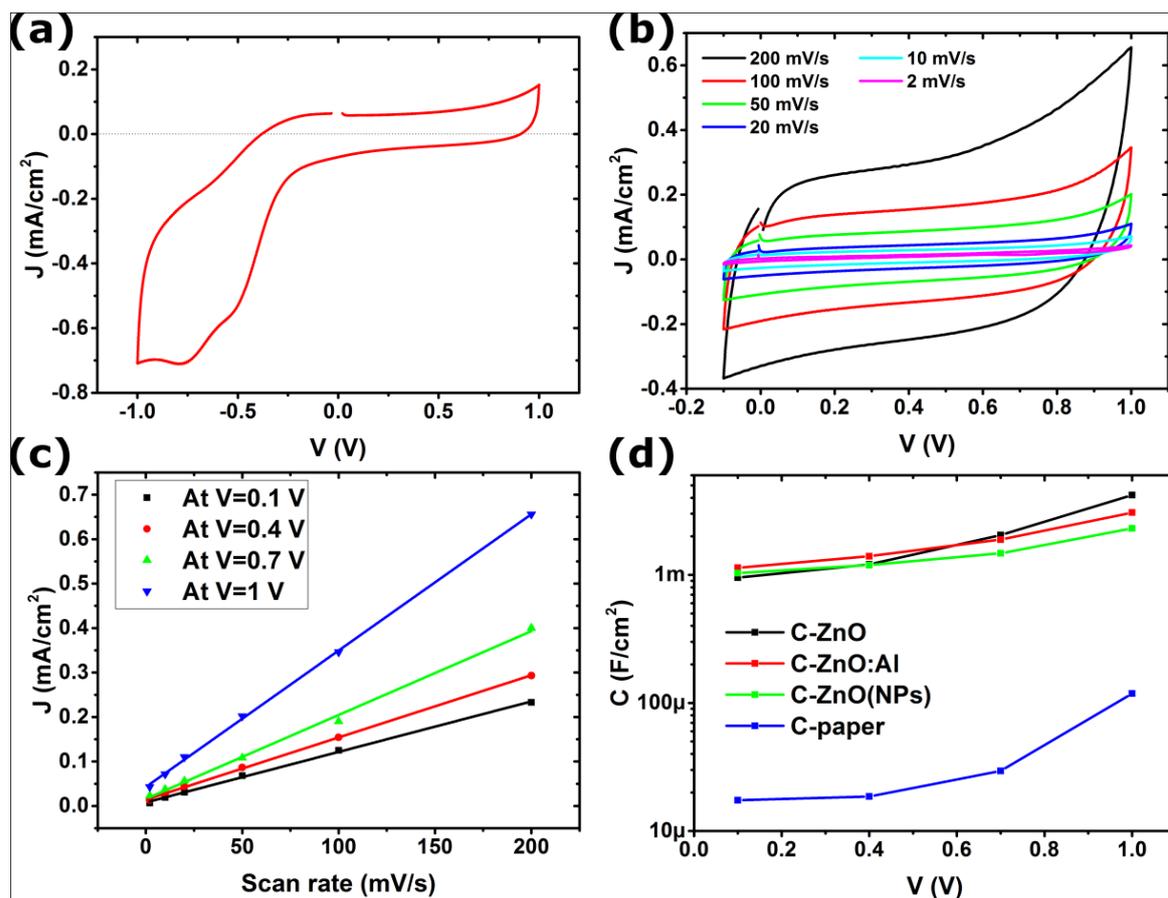
Fig. 5. (a) Cyclic voltammogram of a C-ZnO electrode at 100 mVs^{-1}. (b) Cyclic voltammograms of the best CDI nanocomposite (C-ZnO electrodes, Fig. 3 above) at different scan rates. (c) Current density versus scan rate for the sample in (b) for four different electrode potentials. (d) The calculated specific capacitance of all four investigated CDI nanocomposite electrodes, dipped into reference saline water, versus voltage. The best nanocomposite electrode, C-ZnO, is shown as a black trace.

To identify the desalination efficiency of the electrodes from the electrochemical analysis, the consumed energy at each charging half-cycle was compared to the stored charge during the discharging half-cycle. Here, our calculation assumes that all charge stored in the system originates from the accumulation of Cl$^-$ anions at the interface. The reversible charge/discharge mechanism with excellent stability of the materials supports this assumption. Fig. 6(d) shows that about 50 kJ is consumed in our C-ZnO electrode with a 1 cm^2 surface area to desalinate one mole of Cl$^-$ anions in an aqueous electrolyte. To confirm the desalination efficiency of commercial CDI cells, larger electrodes are required. Moreover, an accurate system for circulating the saline water is needed.

Furthermore, in an attempt to fabricate nanocomposite counter electrodes for capturing the cations (Na$^+$), we protected the C-ZnO electrodes with an innovative ionic polymer electrolyte (IPE) consisting of PEO and PVP polymers, mixed with InAs nanowires. Despite a successful electrode fabrication, the developed IPE was not stable enough in the aqueous solution due to the solubility of one of the polymers. Fig. 7 compares the reduction in the capacitance of the protected electrode (C-ZnO/IPE) compared to a C-ZnO electrode.
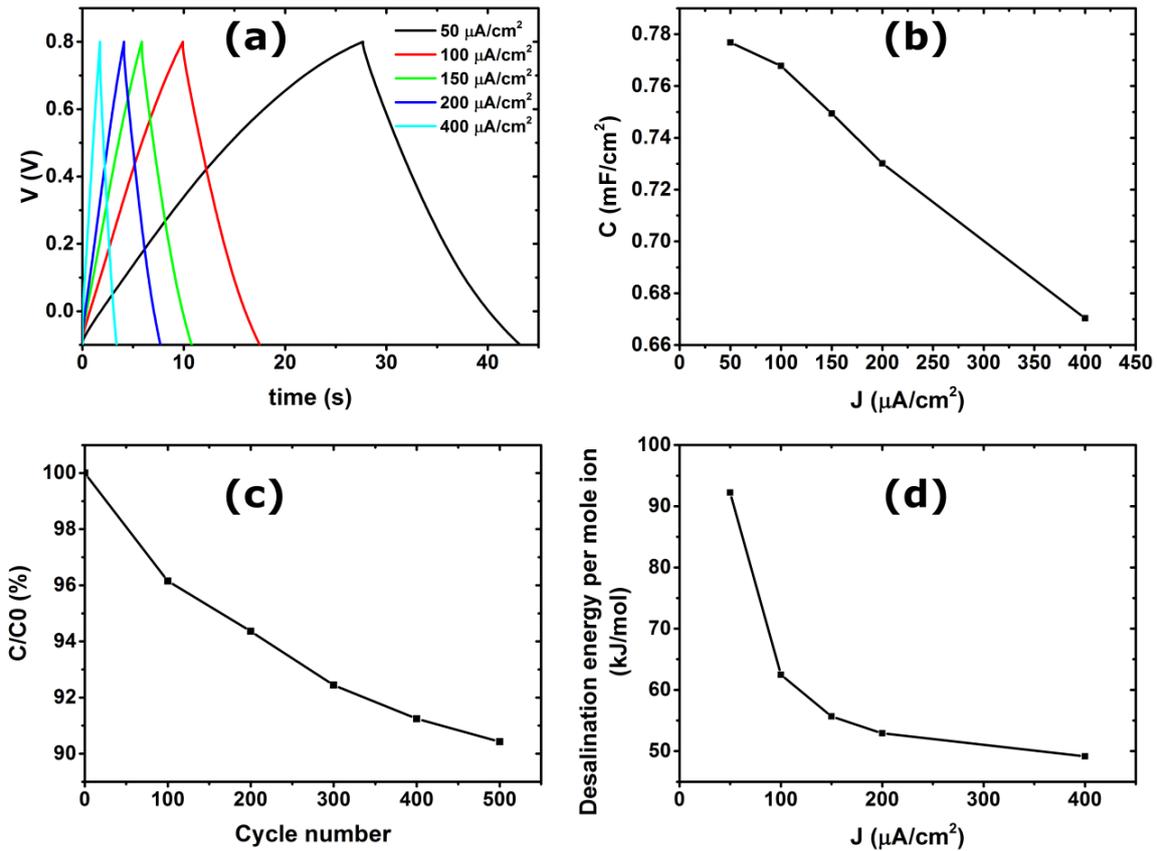
Fig. 6. (a) Chronopotentiometry charge/discharge curves of a C-ZnO electrode for different current densities. (b) Specific capacitance – current density dependence of the C-ZnO electrode. (c) Capacitance stability after 500 cycles of charging and discharge at ±200 µA.cm^{-2}, respectively. (d) Calculated desalination energy consumption per mole ion of a saline NaCl solution.
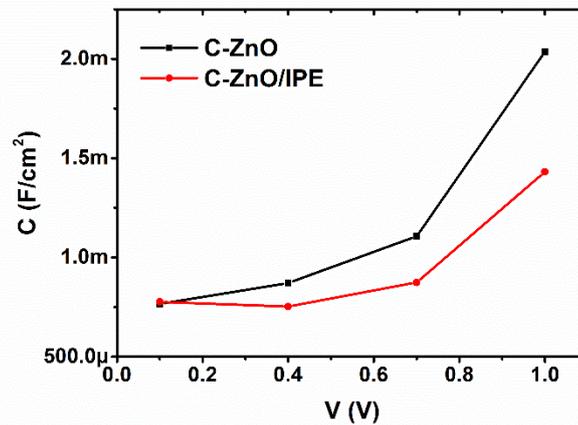

Fig. 7. A comparison of the specific capacitance of the C-ZnO electrode and the electrode protected with the ionic polymer electrolyte (C-ZnO/IPE) in the same aqueous solution.

IV.   Conclusions and Outlook

The experimental results obtained in this project clearly demonstrate that the developed CDI electrodes are indeed very promising for water desalination. The dissociated Cl$^-$ anions in the saline water are efficiently captured at the optimized C-ZnO electrodes forming a double-layer supercapacitor. Furthermore, the ion species are not chemically bound to the electrodes,

which indicates that no undesired redox reactions occur. Hence, the electrodes are regenerative (i.e., can be cleansed) by reversing the polarity of the applied bias. The C-ZnO electrodes showed excellent stability after a 500-cycle desalination operation. The highest desalination energy efficiency of 50 kJ/mol was calculated for the best nanocomposite electrodes. In this work, C-ZnO/IPE electrodes were also developed for storing cations (Na^+), needed to fabricate a complete CDI cell. In this case, however, further studies are needed to develop a suitable electrode working in the negative voltage range without degrading.

We intend to continue this very promising development of fully operational CDI cells with funding from other sources, e.g., Vinnova, patent our nanocomposites and possibly start a company. We are presently finalizing a manuscript that will be submitted to the high-impact journal *Desalination* (https://www.journals.elsevier.com/desalination).