

Polymer-coated composite anodes for efficient and stable capacitive deionization



X. Gao^a, A. Omosebi^a, N. Holubowitch^a, A. Liu^{a,b}, K. Ruh^{a,c}, J. Landon^{a,*}, K. Liu^{a,d,**}

^a Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA

^b Paul Laurence Dunbar High School, Lexington, KY 40513, USA

^c Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

^d Department of Mechanical Engineering, University of Kentucky, Lexington, KY 40506, USA

HIGHLIGHTS

- Polymer-coated carbon anodes were prepared for CDI testing.
- Improved salt removal using polymer-coated anodes was observed.
- Parasitic reactions were discussed based on the pH and steady-state current.

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ABSTRACT

In the contemporary literature, diminished salt removal in a CDI device is primarily due to carbon oxidation at the anode in aqueous solutions. Therefore, an anion exchange polymer is used to prepare a composite carbon as a CDI anode. Results from repetitive CDI testing shows that more efficient and consistent long-term salt removal is achieved when a flow-through CDI stack is configured with composite anodes compared to polymer-free anodes. Analysis of the effluent pH and steady-state current indicates that this performance improvement may be due to the minimization of parasitic reactions by shielding of the carbon electrodes with the selective polymer layer coated at the anode.

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1. Introduction

In the past few decades, various desalination technologies have been developed, among which distillation, reverse osmosis, and electrodialysis are the most commonly known and commercially widespread [1]. Capacitive deionization (CDI) is an alternative and energy-efficient technology for water desalination that utilizes an electrochemical flow cell configured with polarizable porous carbon electrodes to remove ionized salts in a stream with lower molar concentration [2].

In contemporary CDI literature, diminished salt removal in a CDI device during long-term or repetitive operation is one of the remaining issues needing to be addressed. Performance degradation is primarily

accounted for by negative surface charges, e.g., -COO^- , that form via carbon oxidation in aqueous solutions, leading to the positive shifting of the potential of zero charge (E_{PZC}) of the anode [3,4]. Regardless of the carbon electrodes used in these studies, the emergence of inverted behavior is typically observed in the form of salt desorption peaks at the beginning of the charging steps (see Fig. 2a), which is detrimental to the equilibrium salt removal capacity for a CDI device [5,6]. Recently, the formation of these inversion peaks was theoretically described by the modified Donnan model by introducing a term for chemical surface charge [7]. It is becoming increasingly clear that fixed surface chemical charges (or charge barriers) play a critical role in CDI, which is supported in ref. [8–15].

Previous efforts to extend the longevity of a CDI device include the reversal of polarization, the reduction of applied voltages, and the use of selective exchange membranes [3,16]. In this work, we show that a protective layer prepared from anion exchange polymer powder imbues CDI anodes with oxidation resistance. Results from repetitive

* Corresponding author.

** Correspondence to: K. Liu, Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA.

E-mail addresses: James.Landon@uky.edu (J. Landon), Kunlei.Liu@uky.edu (K. Liu).

charging and discharging of flow-through CDI stacks with and without composite anodes demonstrate the efficacy of the protective polymer layer. Additionally, pH behavior and the E_{PZC} are invoked to explain the performance enhancements.

2. Experimental

2.1. Electrode preparation and characterizations

The polymer casting solution was prepared using anion exchange powders, *n*-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich), and polyvinylidene fluoride (PVDF) (Sigma-Aldrich) with a mixture ratio of 12:20:1 by weight. The anion exchange powder was prepared from a type 1 strong base anion resin with trimethylamine functional groups (chloride form, SBG1-F, ResinTech, Inc.) in a planetary mill (Fritsch Pulverisette). The resulting solution was brush-painted onto both sides of pristine Spectracarb 2225 carbon cloth (Pr-SC) (Engineered Fibers Technology, LLC), followed by heat treatment at 150 °C for 30 min under vacuum to remove the solvent and set the polymer. The resulting anionic polymer modified carbon was termed A-SC.

Surface morphology was characterized using a scanning electron microscope (SEM) (S-4800, Hitachi). N_2 adsorption/desorption isotherms were measured using a surface area and porosity analyzer (ASAP2020, Micromeritics) with about 0.15 g of sample degassed at 120 °C for 12 h. Cumulative pore volume was calculated via the non-localized density functional theory (NLDFT) provided by Micromeritics. Cyclic voltammograms were recorded using a potentiostat (Reference 600, Gamry) attached to a three-electrode cell containing approximately 0.36 cm² of sample working electrode, a saturated calomel reference electrode (SCE), and a 1.8 cm² carbon counter electrode.

2.2. CDI testing using Stack A and B

A flow-through CDI stack consisting of 16 electrode pairs, an in-line conductivity sensor (Alpha Cond 500, Thermo Scientific), an in-line pH sensor (Alpha pH 500, Thermo Scientific), a polyethylene tank, and a peristaltic pump (Masterflex L/S, Cole-Parmer) were assembled. CDI tests were performed at 1.2 V charging and 0 V discharging (1.2/0 V) in about 31 L of 7 mM deaerated NaCl solution at 80 mL min⁻¹. Two structurally identical CDI stacks with different anodes were used, and the construction of a CDI stack in detail can be found in ref. [17]. Stack A was configured with 16 pieces of the Pr-SC anodes and 16 pieces of

the Pr-SC cathodes while Stack B was assembled with 16 pieces of the A-SC anodes and 16 pieces of the Pr-SC cathodes.

A micrograph of the A-SC anode in Fig. 1(a) shows a combined anionic polymer layer with the Pr-SC carbon cloth. (The micrograph of the Pr-SC has been described in ref. [12]) The Pr-SC carbon cloth is overlaid with a graphite or titanium current collector to carry electric charges in both cyclic voltammetry and CDI tests (see Fig. S8). As depicted in the inserted photograph, the prepared A-SC was cut to a geometric area of $\sim 7 \times 4$ cm² with the anionic polymer layer placed in the center. The A-SC anode including the 6.5×3.5 cm² painted area was paired with the $\sim 7 \times 4$ cm² Pr-SC cathode to configure a CDI cell in the present CDI tests. Additionally, 1 piece of the A-SC anode and Pr-SC cathode had average masses of ~ 0.89 and ~ 0.38 g, respectively.

The total salt adsorption, SA, for Stack A and B was calculated by multiplying the volumetric flow rate, Φ , by the integration of the concentration, c , with time, t , using

$$SA = (M\Phi) \int (c(t) - c_{in}) dt \quad (1)$$

where M is the molecular weight of NaCl (58.44 g mol⁻¹) and c_{in} is the influent concentration. The charge passed, Q , for the charging (or salt adsorption) step was calculated by integration of the current curves with time. Finally, the charge efficiency, Λ , is calculated using

$$\Lambda = (SA F)/(MQ) \quad (2)$$

where F is the Faraday's constant (96,485 C mol⁻¹). Before CDI testing, the NaCl solution was circulated through both CDI stacks at open-circuit voltage until the effluent pH stabilized.

3. Results and discussion

3.1. Electrode characterizations

Cumulative pore volume versus pore size is plotted in Fig. 2(a). A sharp increase in the pore volume up to a pore size of 2 nm indicates that the Pr-SC is a microporous carbon, possessing a total pore volume of 0.84 mL g⁻¹. By comparison, adding the polymer layer results in the total pore volume of the A-SC being reduced to 0.39 mL g⁻¹, however the microporous carbon character is retained. As depicted in Fig. S1(b) and (c), the dried polymer solution (without being painted onto the Pr-SC) has no significant quantity of N_2 adsorption/desorption in its isotherm, meaning that the impact of the polymer layer on the A-SC's total pore volume may be negligible. Therefore, the decreased pore volume of the A-SC in Fig. 2(a) is mainly attributed to the increased weight of the A-SC by the anionic polymer layer, which can be supported by comparing the capacitive behaviors in the corresponding voltammograms normalized by its total pore volume in Fig. S3(b).

As highlighted in Fig. 2(b), the cyclic voltammograms normalized by the geometric surface area of 0.36 cm² show distinct V-shaped regions for both the Pr-SC and A-SC between -0.25 and -0.04 V vs. SCE. At such potential corresponding to the E_{PZC} , these electrodes have the least capability for ion adsorption [18]. It is also found that the capacitive behavior for the A-SC to its V-shape in the cathodic region is significantly diminished, which is due to limited cation adsorption that stems from having an anionic polymer layer over the A-SC. The capacitive behavior for the A-SC to its V-shape in the anodic branch is still as pronounced as the Pr-SC. Thus, we consider that the use of the A-SC anodes paired with the Pr-SC cathodes should be suitable for CDI applications.

In addition, we expect that the SA for Stack B (using the A-SC anodes) should be similar to that for Stack A, as the total pore volume for both of the stacks are almost equal, ~ 10.2 mL for Stack A and ~ 10.6 mL for Stack B, where the total pore volume in a CDI stack was calculated via the weight of the electrodes multiplied by the pore volume for an electrode depicted in Fig. 2(a).

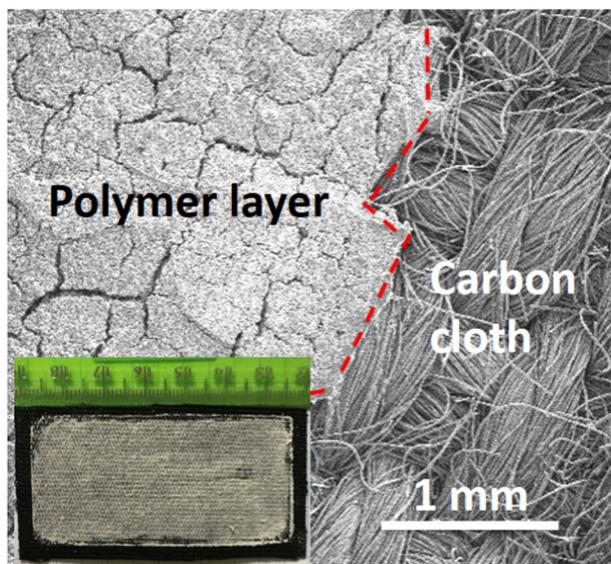


Fig. 1. Micrograph and photograph (inset) of the A-SC anode including a combined anionic polymer layer with the Pr-SC carbon cloth.

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