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Electrically Regenerated Ion-Exchange Technology for Desalination of Low-Salinity Water Sources

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Abstract

A promising approach to increasing freshwater availability is the effective desalination of widely available and abundant low salinity water sources. Here we report a new approach to desalinate low salinity water sources using inexpensive ion exchange resins (IER). IER are widely used for water softening but require regular chemical regeneration. Instead, our proposed approach relies on electrical regeneration of IER by incorporating them into a functional composite material, eliminating the need for regular use of corrosive chemicals. We report proof-of-concept results and demonstrate reliable regeneration of IER-composite electrodes using a lab-scale prototype device. With further characterization and development, this new approach offers a path to distributed deployment of IER for desalination of low salinity water sources.

Keywords: ion-exchange resin, electrical regeneration, composite electrode, brackish water, desalination

1. Introduction

Only 2.5% of all global water supply is freshwater. Much of it (about 70%, or 1.8% of total) is frozen in the cryosphere [1], and the rest is highly unevenly distributed. With a steady increase in population and global prosperity, and with climate change, this limited freshwater resource is becoming increasingly insufficient [2]. According to the United Nations, currently 20% of the global population (1.4 billion people) experience freshwater scarcity and by 2025 1.8 billion people will experience extreme water stress [3]. Considering that nearly all human activity (e.g. agriculture, industrial manufacturing, community development) relies on availability of freshwater, it is critical to address the growing freshwater shortage. A

comprehensive approach to meeting the growing freshwater demands requires not only the efficient use and conservation of existing freshwater resources, but also the implementation of desalination technologies to generate new freshwater supply.

The salinity of a source is quantified in terms of its total dissolved solid (TDS) content reported in ppm. While the desalination of high salinity seawater (35,000 ppm) is energy intensive, theory predicts that the energy required for desalination of low-to-intermediate salinity (1,000-10,000 ppm) sources is significantly less. Such low salinity water sources are widely available, either naturally or as a result of human activity, and are referred to as brackish water. Although there are currently no known health effects of drinking brackish water, sources with TDS >500 ppm have highly undesirable taste making them unpalatable, and WHO drinking water guidelines recommend TDS < 500ppm [4].

Several commercial technologies are available for desalination of brackish sources, however the widespread adoption has been limited due to their high capital cost, regular maintenance needs, high energy demand, or low water recovery rates [5,6]. Theoretical studies have shown charge-based salt separation to be considerably more energy efficient than membrane and thermal-based methods for sources with salinities $\leq 5,000$ ppm [7]. Charge-based desalination technologies currently commercially available include ion-exchange resins (IER), membrane capacitive deionization (mCDI), and electrodialysis (ED). While the theoretical energy-efficiency benefits for charge-based separation technologies (over membrane-based separation) are achieved for source salinities of $\leq 5,000$ ppm, the practical salinity limits are considerably lower. For example, the practical salinity limit for mCDI technology to achieving energy savings over reverse osmosis (RO) has been demonstrated to be just 2,300 ppm[8]. Given that RO is both a mature technology and has reached economies of scale, emerging technologies such as mCDI and ED face tough competition in the brackish water desalination market. On the contrary, ion-exchange is a mature technology that is industrially-scaled, inexpensive, and is well suited for treatment of low-salinity water sources. However, the use of IER for desalination is currently limited, as the technology requires regular use of corrosive chemicals for regeneration.

In order to utilize IER for desalination of low salinity water sources, developing a sustainable alternative to chemical regeneration is critical. Prior studies have explored pressure-driven and thermally-driven regeneration of IER [9–12]. The thermal studies concluded thermal regeneration rates to be inadequate for practical applications if conventional bead sizes are used [9]. The electrical regeneration study focused on selective Cr-ion capture within a ED unit by packing IER between the ion-specific membranes [13] — an approach widely used in commercial continuous electrodeionization (CEDI) units [14]. A more recent study explored IER/carbon-composite electrodes for selective vanadium removal in a capacitive deionization (CDI) unit, but relied on acidic feedwater and acid flushes between cycles for resin regeneration [15]. Further, the use of polymer-composite electrodes to minimize parasitic side reactions in CDI anodes have been reported by Gao et al. [16]. However, the role of ion exchange resins in desalination technologies to date has been limited to either enhancing ion transport (e.g. CEDI) or creating an ion-selective barrier (e.g. CDI, mCDI). Here we propose a third possible role for ion-exchange resins—active material for ion capture. To achieve reversible ion-capture, we rely on electrical regeneration of the insulating resins by embedding them in a conductive matrix.

In this new approach, conductive composites with anion exchange resins (AER) and with cation exchange resins (CER) are used at opposite electrodes within a parallel plate configuration. Within the composite, IER is solely responsible for the capture of salt ions, which occurs with no external voltage applied to the electrodes. Once the IER are saturated with salt ions, however, they must be regenerated for reuse. Normally, IER are regenerated using concentrated acid or base, but in this approach, an external voltage is applied to the electrodes for resin regeneration. The resins are regenerated from a combination of electrostatic repulsion and electrochemical production of regenerant species (H^+ and OH^-) from electrolysis [13,14]. Here we report proof-of-concept results for the approach, which we refer to as Electrically Regenerated Ion-Exchange (ERI) technology.

The ability to capture salt with no applied voltage and to use an applied voltage for electrode regeneration are themselves not unique. Researchers have extensively studied inverse-CDI (also called i-CDI) technology, where chemically modified carbon electrodes passively adsorb salt ions and reject them when a voltage is applied [17–19]. The key difference between ERI technology presented here and i-CDI technology previously reported is the mechanism of salt capture. ERI relies on ion-exchange and not adsorption, so the electrode surface area is not as critical as it is for i-CDI technology, that is adsorption based. Our preliminary results demonstrate the feasibility of ERI approach with inexpensive, low surface area carbon additives (Figure S2). By relying on inexpensive commercial resins and by operating without expensive high surface area carbons, ERI technology offers promise of ultra-low-cost electrodes.

2. Methods

2.1 Materials

AER (Amberjet[®] 4200, OH-form, strong base, gel-type) and CER (Amberlite[®] IR 120 strong acid, gel-type) were purchased from DOW water and process solutions and Sigma Aldrich respectively. Activated carbon (YP-50F) and polyvinyl butyral (Mowital-60HH) were obtained from Kurrary Chemicals. Absolute ethanol was obtained from Alfa Aesar. Food-grade 200 μm thick, polytetrafluoroethylene (PTFE) mesh was obtained from Industrial Netting. Reagent grade sodium nitrate ($NaNO_3$) and DI water were obtained from Sigma Aldrich and VWR, respectively.

2.2 Electrode Preparation

To prepare the two ERI electrodes, separate inks were prepared containing either CER or AER according to the procedure described below. The commercial IER were milled for 5 minutes in a zirconia ball mill container using a Spex[®] Miller 8000M. The electrode inks were prepared by milling a mixture of 1.5 g of milled IER, 0.5 g of carbon, and 4 g of 5wt% PVB binder solution, with either 3 g of ethanol (for CER) or 5 g ethanol (for AER) in a stainless steel ball mill jar for 5 min using a Spex[®] Miller. The ink mixtures were then printed on the 100 cm^2 (10 cm x 10 cm) stainless steel current collectors using an adjustable film applicator (micrometer doctor blade) device and air dried for 30 min. Identical methods were used in case of the carbon-only electrodes except for the replacement of the milled IER in the ink with equal mass of carbon.

2.3 Device Assembly

The stainless steel current collectors coated with a thin-film of the carbon-IER composite electrodes were placed on either end of a Delrin[®] manifold and mechanically held in place. The electrodes were electrically isolated using insulating PTFE mesh.

2.4 Experimental Set-up

The flow diagram of the experimental setup is shown in Fig 1 along with a photograph of the prototype ERI cell. A bulk solution of 10 L of 100 ppm NaNO₃ was circulated through the system. The solution was pumped at a flow-rate of 10 mL/min using a VWR chemical transfer pump. The unit was operated on a 15 min desalination (no applied voltage) and 5 min regeneration (3 V applied voltage) cycle using a DC-power supply (BK-Precision 1785-B). An in-line conductivity meter (Vernier Scientific) was used to measure effluent conductivity. The effluent conductivity as a function of ERI cycling was recorded with an in-house program supported by an Arduino Mega 2560.

2.5 Characterization

Scanning Electron Microscopy (SEM) imaging of the electrodes was conducted using a tabletop FEI- Phenom G1.

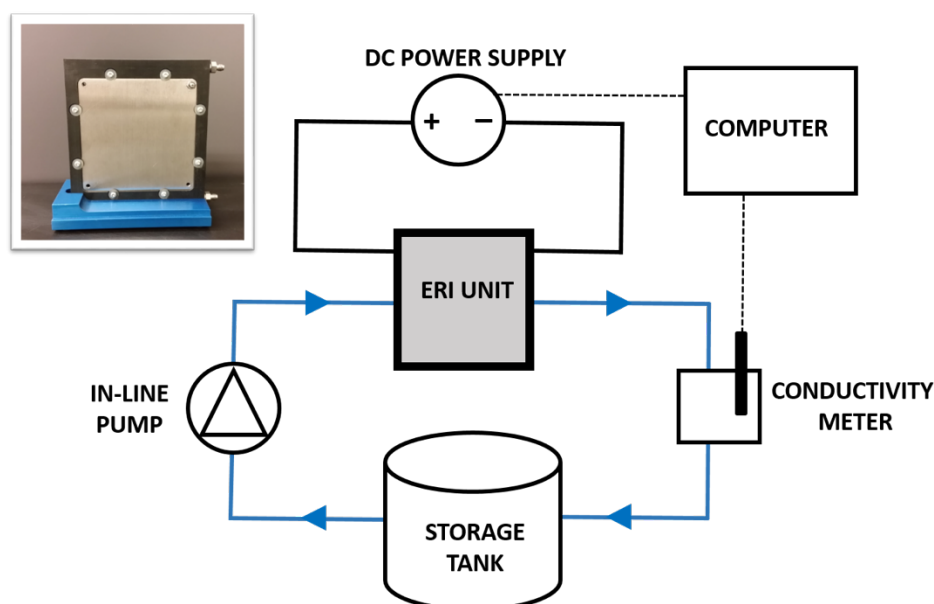


Figure 1. Flow diagram of testing setup. Inset shows a photograph of the ERI prototype.

3. Results and Discussion

3.1 Proof-of-concept

To demonstrate feasibility of ERI approach, electrode mixtures (“inks”) starting from commercial IER were prepared. Electrodes with varying resin to carbon ratio were tested and preliminary performance data (Figure S1) was used to identify a suitable electrode composition (75 wt% IER and 25wt% carbon) for the study. For in-device testing, the liquid inks containing IER, a conductive carbon additive, and binder, was printed as a thin film onto a stainless steel current collector (Fig 2a). Scanning electron microscopy (SEM) images of the composite electrodes (Fig 2b,c) show the average diameter of milled resin to be in the range of 10-20 μm and the cross-sectional thickness of the composite electrodes to be 35-40 μm .

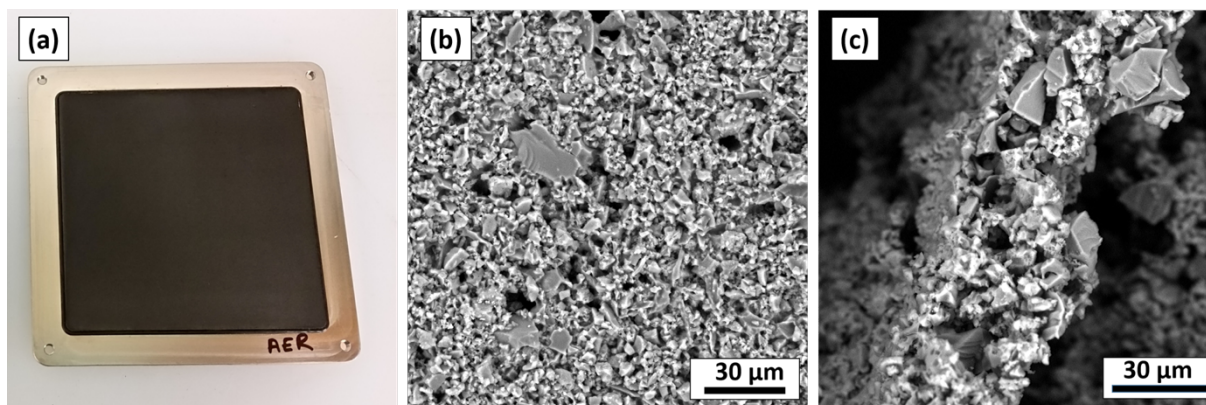


Figure 2. Representative images showing IER-composite electrodes used in ERI technology: (a) photograph of the IER-composite electrode painted on the stainless steel current collector, and SEM images of (b) the top-view, and (c) cross-section view of the IER-composite electrode.

Performance of the ERI unit was tested by cycling between 0V (15min) and 3V (5 min) and measuring the conductivity of the treated effluent. A reservoir of significantly larger volume than that of ERI unit (by 500x) was used for the tests and the feedwater was recirculated through the system (Fig 1). The device was operated continuously for 90 hours. The effluent conductivity vs. time after the system reached stable operation is shown in Fig 3a. The effluent conductivity relative to the feedwater conductivity decreases during desalination as the IER capture the salt ions, and increases during regeneration as the IER release the captured salt ions. Salt removal during the very first desalination cycle using carbon+IER is not a surprise as the electrode operates identical to conventional IER. However, the ability to capture salt over the subsequent cycles is possible only if the resins are successfully electrically regenerated. The sustained desalination capability using ERI approach reported here confirms successful electrical regeneration of IER within the composite electrodes.

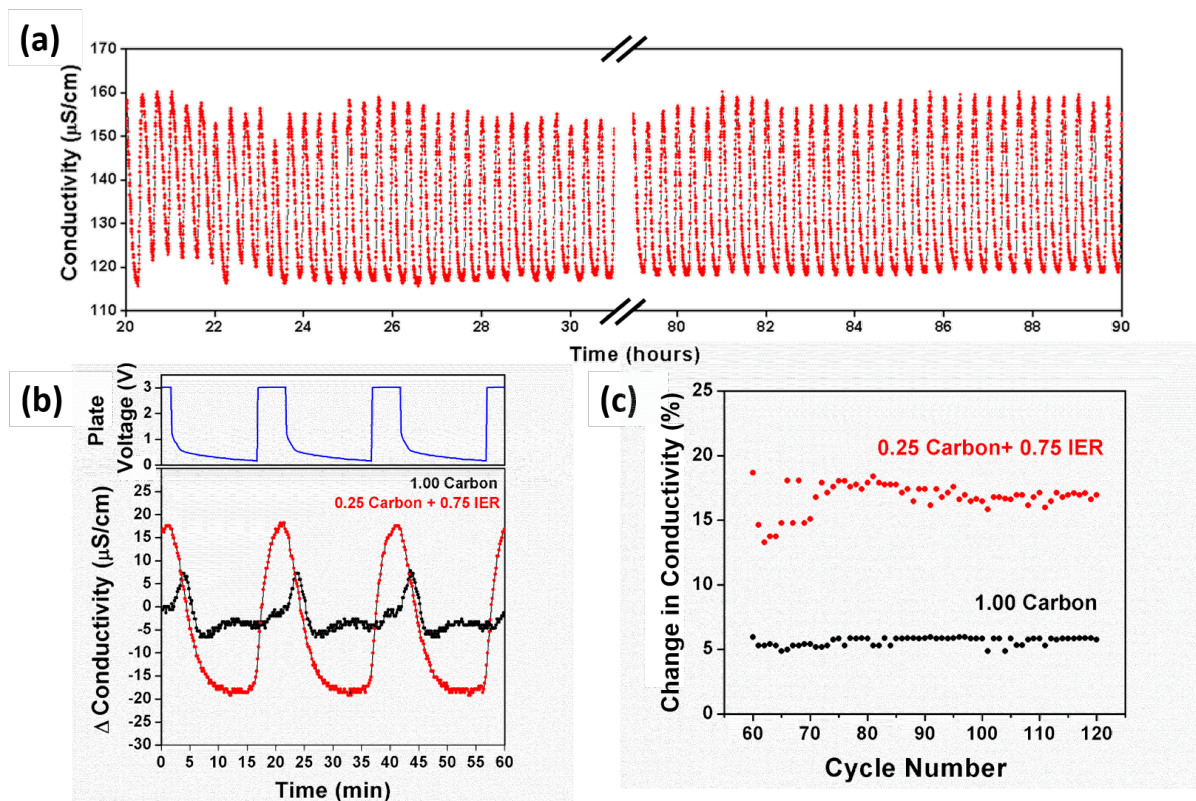


Figure 3. (a) Change in effluent conductivity as a function of time during continuous cycling of the ERI prototype. (b) Comparison of carbon and carbon + IER electrodes tested under identical operating conditions in the ERI unit. (c) Percent change in conductivity per desalination cycle for carbon and carbon+ IER electrodes for 120 cycles. All experiments were conducted with 100 ppm NaNO_3 feedwater and a flow rate of 10 mL/min.

3.2 Carbon vs. resin contribution

To distinguish the contribution of the carbon and the IER to salt removal in the carbon-IER composite electrodes, performance of 0.25 carbon+0.75 IER (weight ratio) electrodes was compared with carbon-only (1.00) electrodes under identical experimental conditions (Fig 3b, 3c). The electrodes were cycled overnight (12h) to reach stable operation before evaluation. The IER-carbon composite electrode showed sustained, higher salt removal capacity compared to the carbon-only electrode, indicating that the IER contributes to salt capture. The difference in salt removal capacities of the electrodes can be assessed from average area under their corresponding desalination curves (Fig 3b). It is important to note that salt removal by the carbon-only electrodes is out of phase with the salt removal by carbon-IER composite electrodes with respect to the zero-voltage and applied-voltage cycles. This out-of-phase performance results from the fundamental difference in the mechanism of salt capture at the two types of electrodes. In the case of the carbon-IER electrode, salt capture occurs with no applied voltage. IER containing H^+ or OH^- ions exchange them for the Na^+ or NO_3^- ions in solution due to a combination of ion selectivity, that is inherent to the resins, and salt concentration gradient between the solution and the resin. In the case of the carbon-only electrodes, salt capture occurs due to capacitive adsorption of ions once the external voltage is applied, and salt-release (instead of salt-capture) occurs during the zero-voltage phase. Here we like to note that the behavior of carbon only electrodes (Fig 3b) is slightly different from

that observed in a CDI system. This difference is likely a result of considerably higher voltages used here (3V) compared to CDI systems (1.2 V). To confirm that the observed salt capture is unrelated to the high surface area of the carbon additive, the feasibility of the approach was tested both with a high surface area carbon (YP-50F, 1660m²/g) and a low surface area carbon (Super-P, 62m²/g). The resulting electrodes show a lack of clear connection between ERI electrode performance and the specific surface area of the carbon additive (Figure S2). Identifying the optimum carbon properties and loading to maximize salt capture capacity of ERI electrodes requires further research.

3.3 Long-term cycling

The carbon and carbon+IER electrodes were tested for 120 cycles. The maximum decrease in conductivity measured during the desalination phase of each cycle is plotted as percent change relative to the feedwater conductivity in Fig 3c. Although carbon+IER electrodes show varying performance in earlier cycles, the variability is significantly reduced over time. Further, the carbon-IER electrodes consistently show about 10-12% higher drop in conductivity per cycle compared to the carbon only electrodes. Given that carbon is considerably less dense than IER, and that our electrodes were prepared based on a carbon to IER by weight ratio, we believe there are opportunities for further enhancing the performance of our ERI electrodes.

3.4 Performance evaluation The parallel plate configuration of the prototype used in this study is similar to water treatment technologies such as ED and CDI, but the salt capture mechanism of ERI is tied to conventional ion-exchange resins. Therefore, a performance comparison of ERI electrodes to the performance of the parent, commercial IER is most meaningful. Based on the average electrode mass, the fractional IER composition of the electrodes, and the measured salt capture performance we estimate that ERI electrodes reproducibly show 25-30% of the salt removal capacity of the commercial precursor IER. The energy consumption of ERI is estimated be 150 kT/ion. Given that these results are preliminary and that the operational cycles and electrode materials are not optimized for maximal salt capture, we envision making considerable performance gains in terms of electrode capacity and ERI energy use with further research.

4. Conclusions

We successfully developed composite electrodes based on commercial IER to demonstrate the feasibility of the electrically regenerated ion-exchange (ERI) approach. Cycling the ERI electrodes in a prototype unit showed long term stability and consistent salt removal upon continuous operation, and ERI electrodes showed higher salt removal capacity than carbon-only electrodes. While these results are preliminary, they demonstrate a promising new desalination approach for low salinity water sources. Future work will address electrode and system optimization, as well as studies to further elucidate salt capture and rejection mechanisms occurring at the electrodes. A detailed techno-economic analysis of the ERI approach is critical to identify viable applications of the technology over conventional IER.

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Supplementary Information

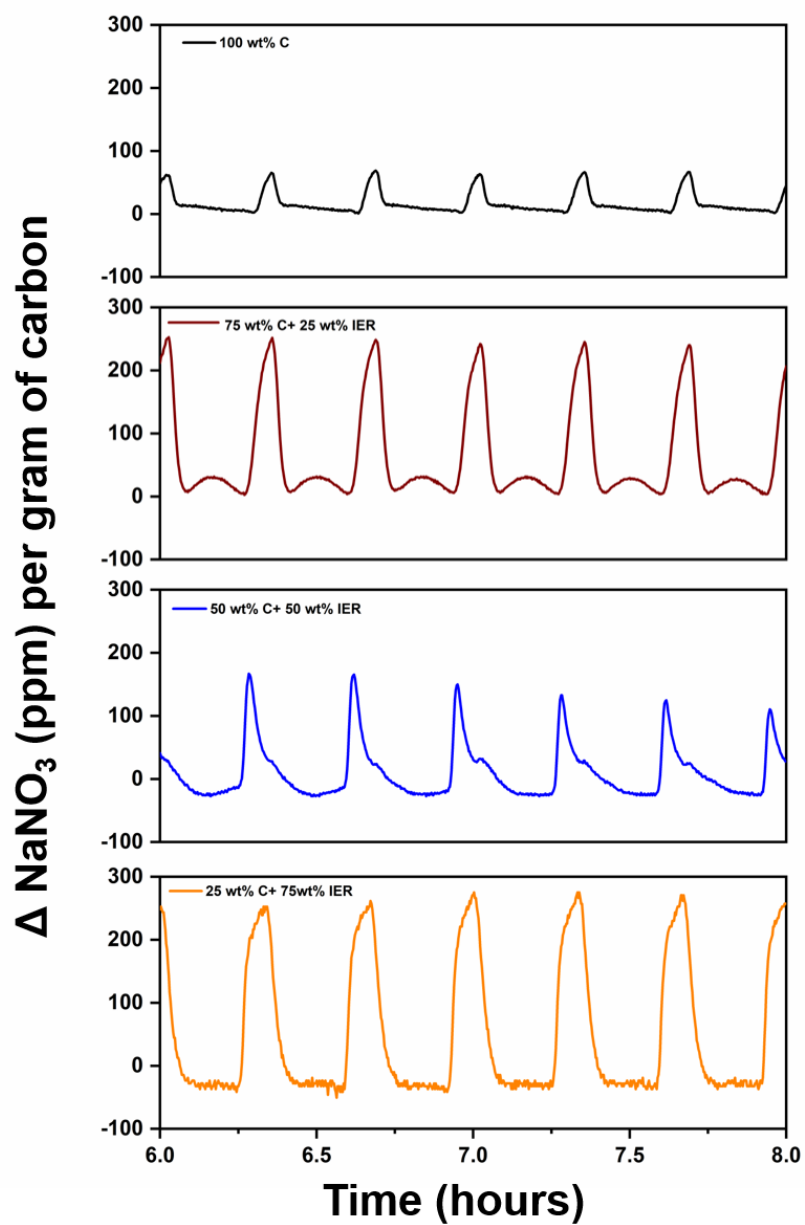


Figure S1. Preliminary data from ERI cycling for various electrode compositions. These results were used to broadly determine the electrode composition used in the study.

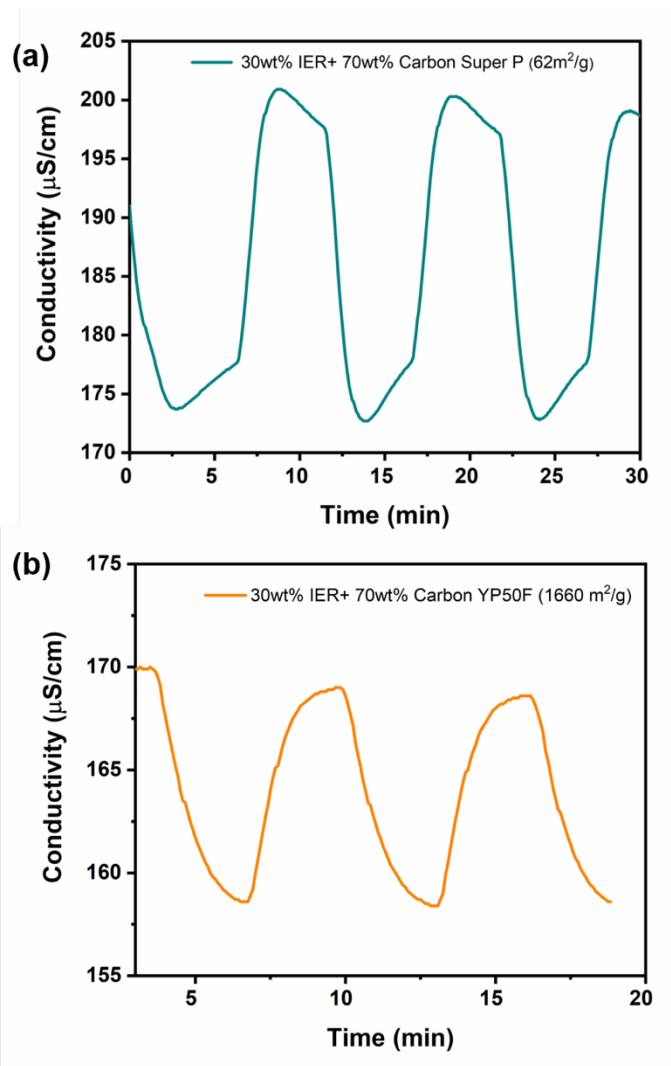


Figure S2. Comparing the performance of ERI electrodes with equal weight percent of carbon additives: (a) low surface area (Super-P, $62\text{m}^2/\text{g}$) carbon and (b) high surface area (YP50F, $1660\text{m}^2/\text{g}$) carbon.