



Supporting Information

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A Covalently Integrated Reduced Graphene Oxide–
Ion-Exchange Resin Electrode for Efficient Capacitive
Deionization

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Characterization of starting materials

Before starting the electrode fabrication method, graphene oxide (GO) was synthesized (detailed protocol has been provided in the experimental section), and it was characterized through spectroscopy (UV-vis and Raman) and transmission electron microscopy (TEM) techniques. Characterization results are shown in Figure S1. In the UV-vis spectrum, two characteristic features of GO were observed at ~ 310 and 235 nm, which are ascribed to the π^* and $\pi\text{-}\pi^*$ resonances, respectively (Figure S1A). The Raman spectrum of the GO sample is shown in Figure S1B, which has two significant peaks at 1350 and 1596 cm^{-1} , corresponding to the D- and G-bands, respectively. Usually, G- and D-bands signify sp^2 hybridization (graphitic signature of carbon) and disorderness of the sp^2 hybridized hexagonal sheet of graphenic carbon, respectively. The G- and D-bands lie in the range of $\sim 1500\text{-}1600\text{ cm}^{-1}$ and $\sim 1300\text{-}1400\text{ cm}^{-1}$, respectively. The D-band's peak intensity and line-width are larger than the G-band in GO, indicating higher disorder, which could be attributed to intense chemical treatments and/or increased amorphous carbon content (unreacted graphite powder). Thus, the Raman spectrum confirms the presence of a graphitic signature of carbon (in-plane sp^2 carbon) and defects present in GO sheets (sp^3 carbon). High-resolution TEM (HRTEM) images of GO at lower and higher magnifications are presented in Figure S1C and Figure S1D, respectively. The HRTEM images revealed a few-layered structure with nearly transparent, wrinkled, and folded GO sheets.

Chemical functionalization of rGO was confirmed using spectroscopic techniques such as UV-vis, Raman, and FT-IR. HRSEM and TEM investigated the electrode material. Energy-dispersive spectroscopy (EDS) analysis further confirmed the chemical composition of the electrode materials. UV-vis spectra of PS, rGO, and rGO-PS are shown in Figure S2A. The characteristic peaks of PS were observed at 273 and 287 nm, which could be attributed to the isolated phenyl groups and interactions between them, respectively [Figure S2A(i)].^[1] A

significant peak appeared at 277 nm in Figure S2A(ii), which corresponds to the feature of pristine rGO.^[2] However, two new prominent peaks at ~270 and ~290 nm were also witnessed for rGO-PS composite, indicating an interaction between rGO and PS. The presence of both rGO and PS features in the UV-vis spectra suggests the formation of the rGO-PS composite [Figure S2A(iii)]. Raman spectra of PS, rGO, and rGO-PS are shown in Figure S2B. Peaks at 846, 898, 980, 1063, 1192, and 1217 cm^{-1} are similar to the Raman features of PS, as observed in Figure S2B(i).^[3] The peaks at 980 and 1063 cm^{-1} correspond to the aromatic C-C stretching of benzene rings of polystyrene. In contrast, mono-substituted benzene rings of polystyrene were confirmed by two peaks observed at 1192 and 1217 cm^{-1} . Figure S2B(ii) shows the Raman spectrum of bare rGO depicting the characteristic features of G- (1580 cm^{-1}) and D- (1331 cm^{-1}) bands, which signifies sp^2 hybridization of graphitic carbons and defect-induced disorder on the sp^2 hybridized hexagonal sheets of carbon. In Figure S2B(iii), the Raman spectrum of the rGO-PS composite is shown with peaks at 973, 1007, 1105, 1141, 1317, and 1577 cm^{-1} . In the same spectrum, no significant shift was observed in the peak position of the G-band of rGO-PS, while the position of the D-band showed a considerable change of 14 cm^{-1} compared to that of pristine rGO. This could be due to the polymeric chains of PS attached to the oxygen-functionalized edges of rGO.

Elemental compositions of both +ve and -ve EAIERs are shown in Figure S3. The SEM EDS of +ve EAIERs confirms C, O, and S as the elements in it (Figure S3A), where the S peak is due to $-\text{SO}_3$ functionality that might be formed after the sulfonation of EAIERs. Similarly, Figure S3B shows the elemental mapping of -ve EAIERs, which confirms carbon and oxygen as the same electrode material's main constituents. The presence of trace amounts of N and Cl is due to the formation of the chloro-aminated product of -ve EAIERs.

The EDS spectra and corresponding elemental maps of both anode (-ve EAIERs) and cathode (+ve EAIERs) are shown in Figure S4A,B. Fluorine was evident in both electrodes due to PVDF, which was used as a binder (~15 wt%) and active materials (EAIERs) during

the fabrication of electrodes on graphite substrates. The presence of C, O, F, and a small amount of N and Cl in EDS confirmed the chemical composition of -ve EAIERs (Figure S4A). The presence of trace amounts of S along with C, O, and F confirmed the chemical composition of +ve EAIERs (Figure S4B). The presence of aluminium (Al) in the EDS spectrum is due to the SEM stub.

Surface charges of both +ve and -ve EAIERs were confirmed by zeta potential measurements. The zeta potential values for +ve and -ve EAIERs were found as -11.1 and -28.4 mV, respectively, and the zeta potential of bare rGO was measured as -24.5 mV. These values further confirm the selective functionalization of both the electrode materials.

FT-IR spectra of electrode materials in details

FT-IR spectrum of PS (Figure 2A) shows a broad peak around 3450-3520 cm^{-1} due to O-H's stretching, which indicates the presence of hydroxyl groups in the electrode materials. This O-H vibrational feature may be due to either (i) the moisture adsorbed on electrode materials or (ii) the presence of NaOH that was used for the activation of styrene during the polymerization process. A characteristic peak at 3035 cm^{-1} was observed due to the aromatic C-H stretching vibration. The other signature peaks at 2925 and 2850 cm^{-1} are ascribed to the asymmetric and symmetric stretching frequencies of aliphatic C-H, respectively. The peaks at 1632 and 1450 cm^{-1} are due to C=C stretching and C-H deformation, respectively. In addition, the IR spectra of both rGO and rGO-PS are shown in Figure 2B. FT-IR spectrum of rGO has been reported earlier.^[4] The peaks at 2924 and 2854 cm^{-1} of rGO are assigned to asymmetric and symmetric stretching of C-H bonds, respectively. The peak at ~1740-1745 cm^{-1} is associated with C=O stretching of the carboxylic acid group. The peak at ~1634 cm^{-1} is due to the C=C stretching frequency of rGO. The spectrum of rGO-PS showed a peak at 2968 cm^{-1} , assigned to aromatic C-H vibration. The characteristic peaks at 2922 and 2852 cm^{-1} are due to asymmetric and symmetric stretching of aliphatic C-H, respectively. The peak at

1631 cm^{-1} is due to the C=C stretching of rGO-PS. A substantial increase in the peak intensity of C=C was observed in the rGO-PS composite, owing to the covalent linkage between rGO and PS, which confirms the rGO-PS composite formation. Figure 2C(iii) shows the FT-IR spectrum of rGO-PS-SO₃H (+ve EAIERs). Peaks at 2925 and 2852 cm^{-1} are the characteristic features of asymmetric and symmetric stretching frequencies of aliphatic C–H bond of +ve EAIERs, respectively, and the other two peaks at 1224 and 1180 cm^{-1} are associated with the S=O bond of SO₃H in the same electrode. Figure 2D(ii) displays the IR spectrum after chloromethylation of rGO-PS composite, which showed two peaks at 2923 and 2851 cm^{-1} indicating the C–H stretching (asymmetric and symmetric, respectively) of rGO-PS-CH₂Cl. The remaining two prominent peaks in the same spectrum at 1411 and 1261 cm^{-1} are assigned to the bending vibrations of aliphatic C–H in chloromethyl –CH₂Cl and aromatic C–H of Ph–CH₂Cl groups, respectively. The FT-IR spectrum of rGO-PS-CH₂–N⁺(CH₃)₃Cl[–] (–ve EAIERs) in Figure 2D(iii) has a peak at 2962 cm^{-1} due to aromatic C–H whereas, peaks at 2924 and 2851 cm^{-1} are due to asymmetric and symmetric vibrations of aliphatic C–H, respectively. The peaks at 1638 and 1632 cm^{-1} confirm the C=C stretching frequency of both –ve EAIERs and rGO-PS-CH₂Cl, respectively. After the chlorinated product's amination, two new peaks were observed at 1208 and 1154 cm^{-1} , which are assigned to the C–N stretching frequencies of the tertiary amine group in -ve EAIERs.

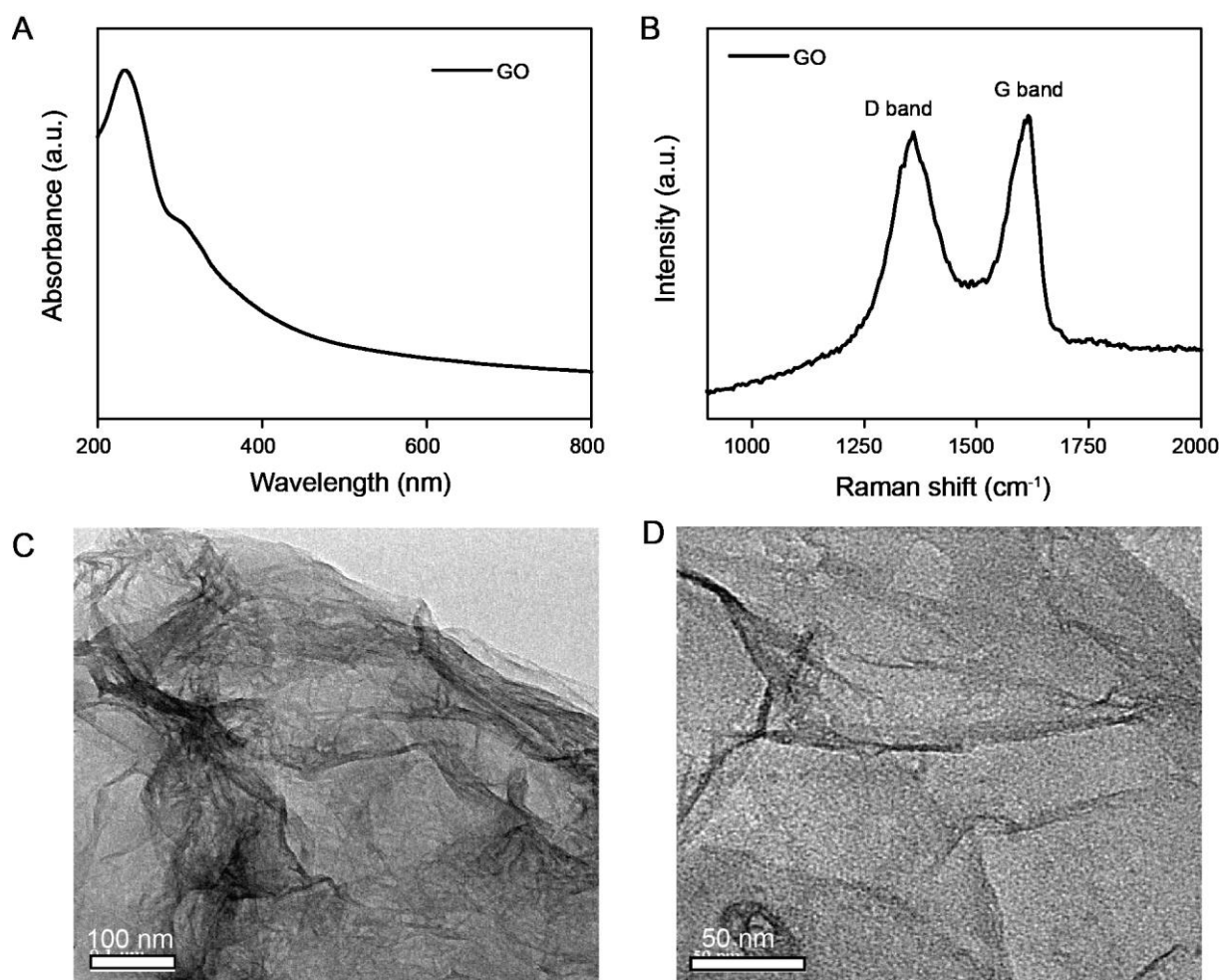


Figure S1. (A) UV-vis spectra of aqueous GO dispersions are presented, (B) Raman spectrum showing the presence of D, G bands, (C) and (D) TEM image of the GO at different magnifications (0.1 μm and 50 nm scale bar, respectively).

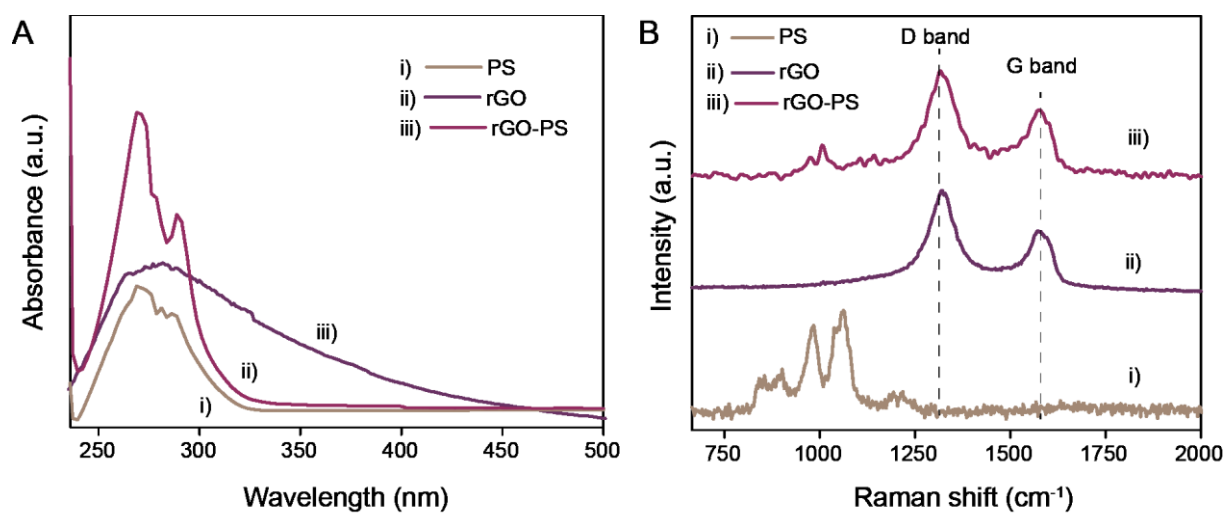


Figure S2. (A) UV-Vis absorption spectra of i) polystyrene (PS), ii) rGO, and iii) rGO-PS composite and (B) Raman spectra of i) PS, ii) rGO, and iii) rGO-PS composite.

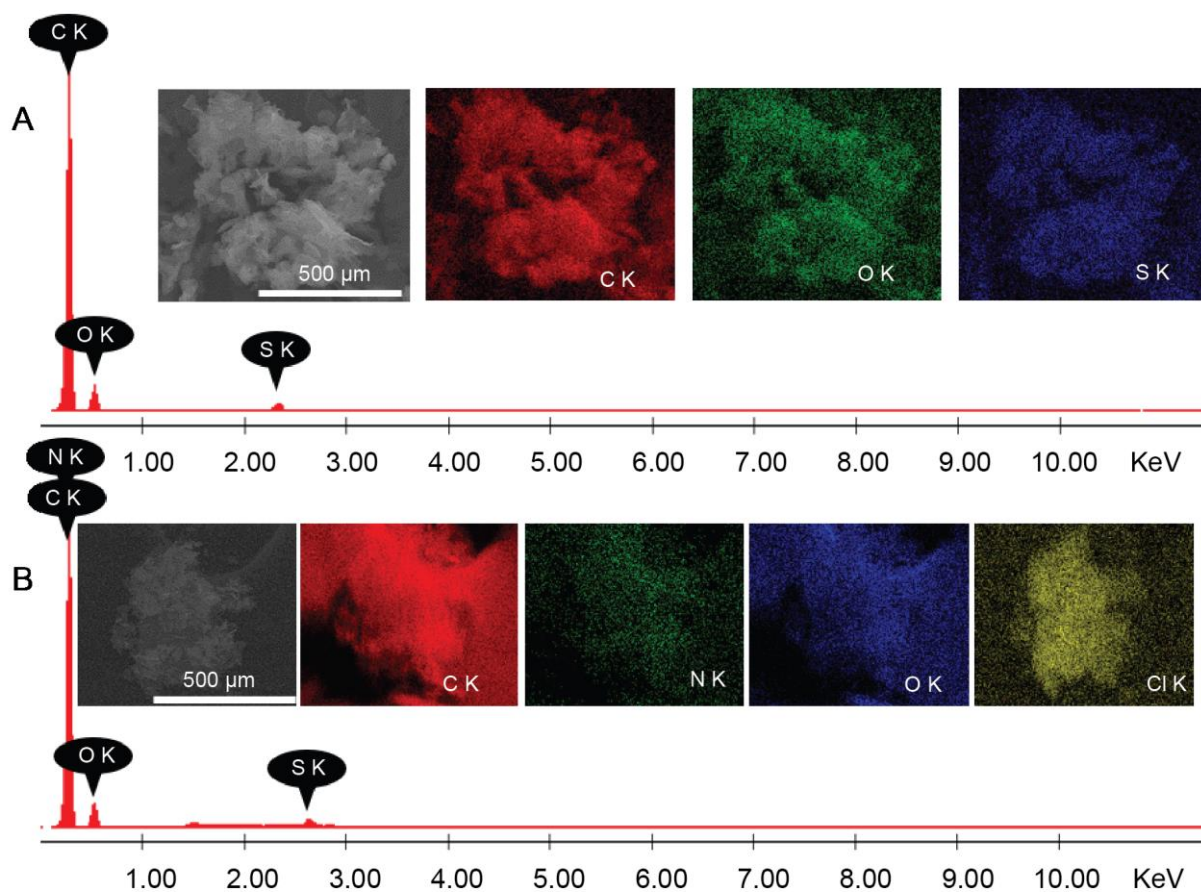


Figure S3. SEM EDS of rGO-PS functionalized ion exchange resin materials of (A) +ve EAIERs (cation EAIERs) and (B) -ve EAIERs (anion EAIERs). The corresponding SEM EDS and elemental mapping images are shown in the inset.

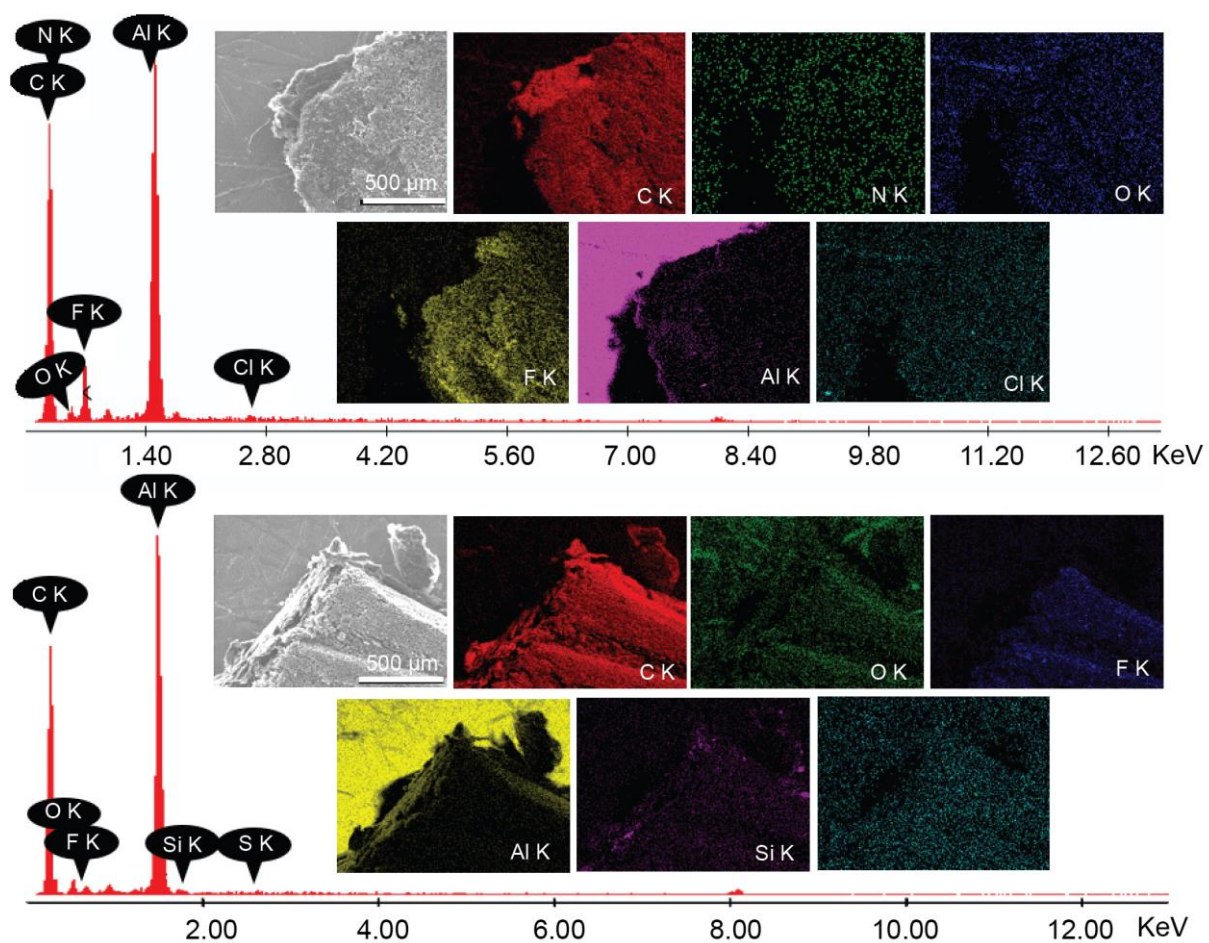


Figure S4. SEM EDS of (A) anode and (B) cathode (before adsorption). The SEM image and the corresponding elemental mapping images are shown in the insets. Aluminium is from the SEM stub.

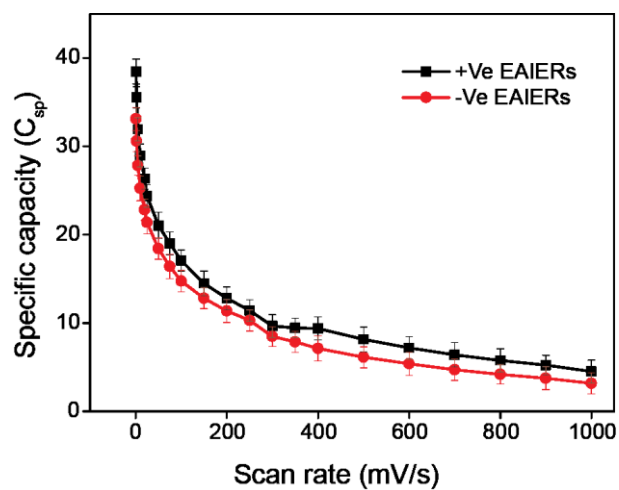


Figure S5. Specific capacitance vs. scan rate for both +ve and -ve EAIERs electrode materials in 1 M NaCl solution.

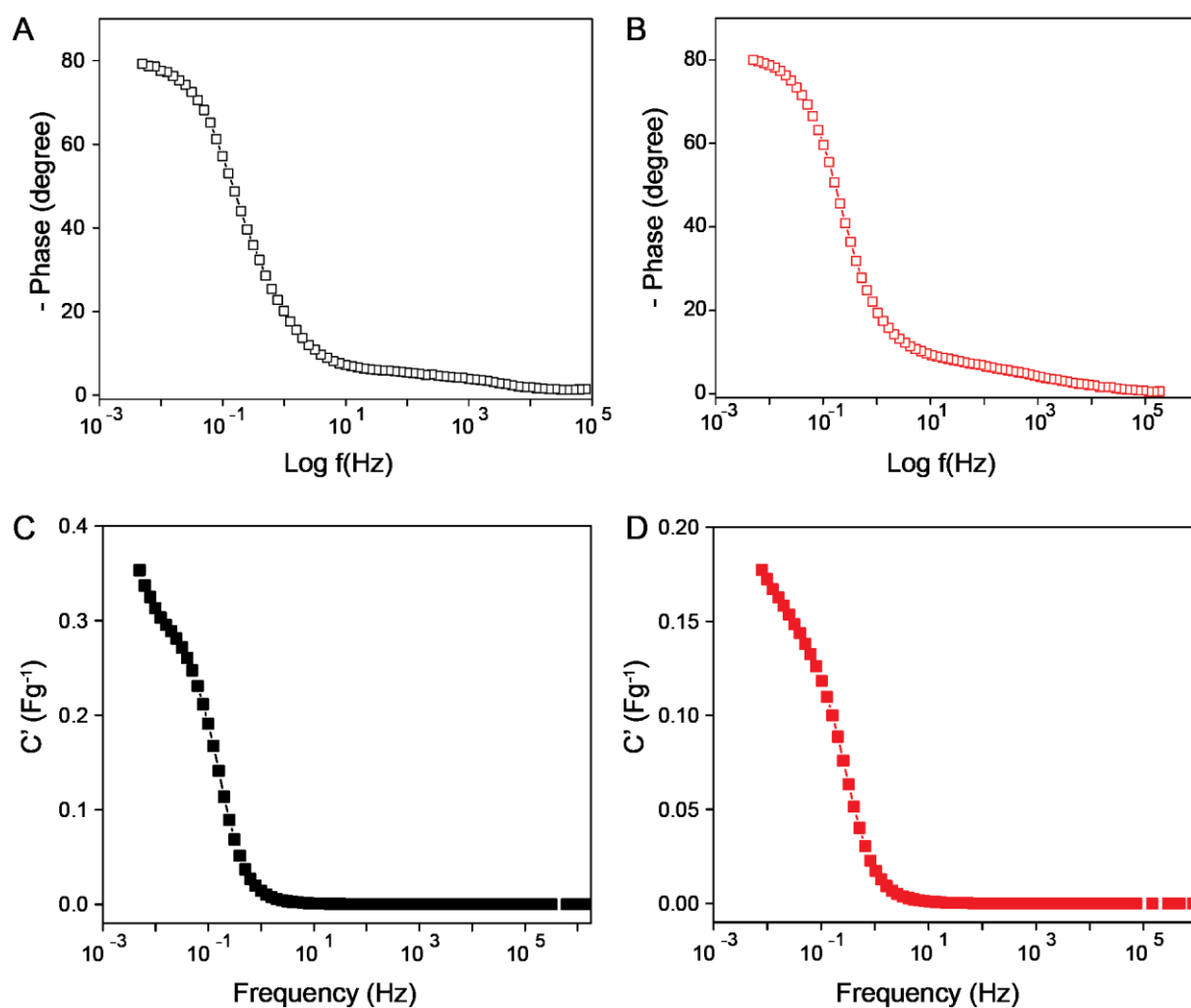


Figure S6. (A) and (B) are Bode impedance for cathode and anode, respectively; (C) and (D) real part of complex capacitance (C') vs. frequency for cathode and anode, respectively; in 1 M NaCl electrolyte.

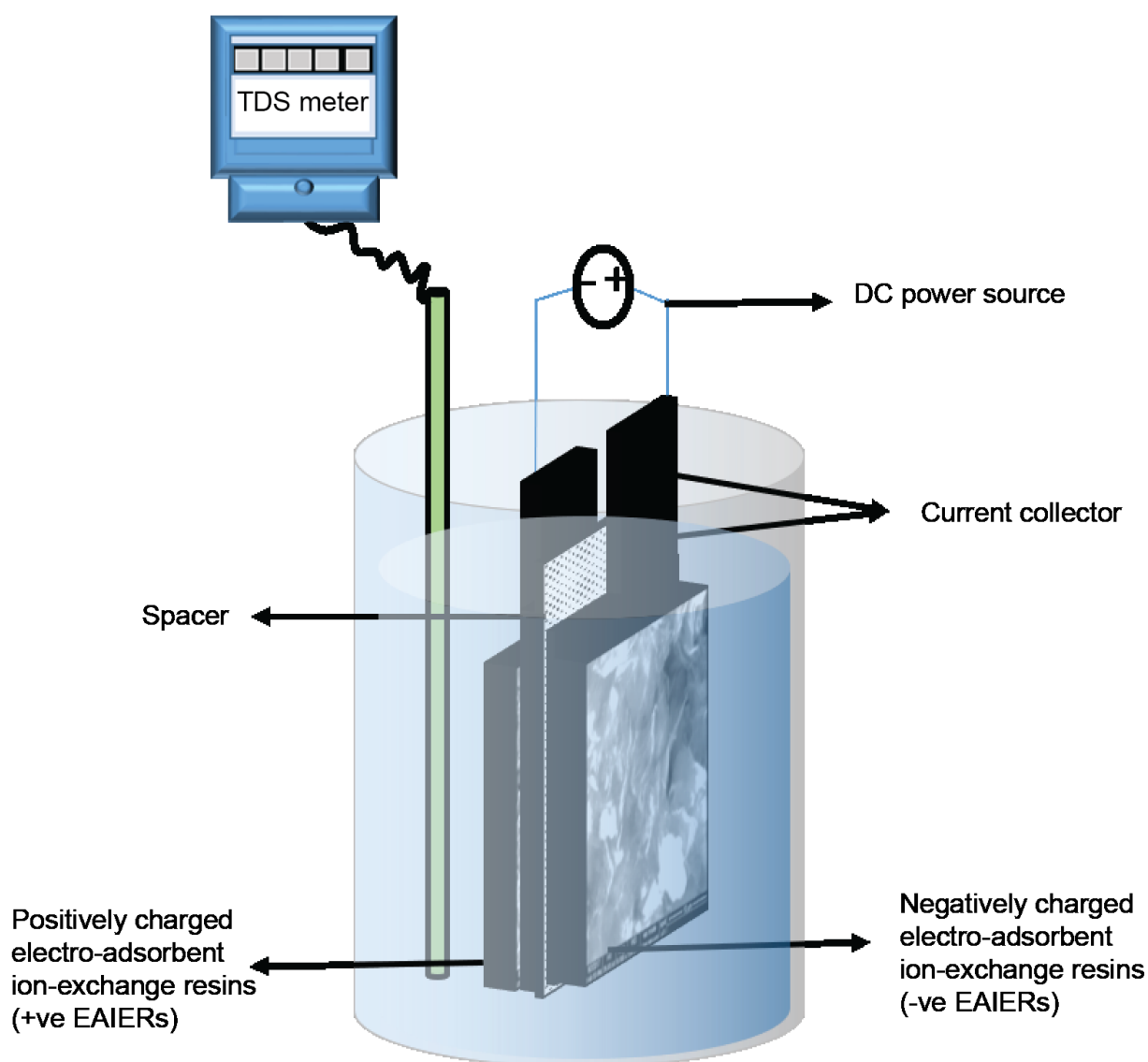


Figure S7. Schematic representation of a CDI set-up used for measuring CDI performance.

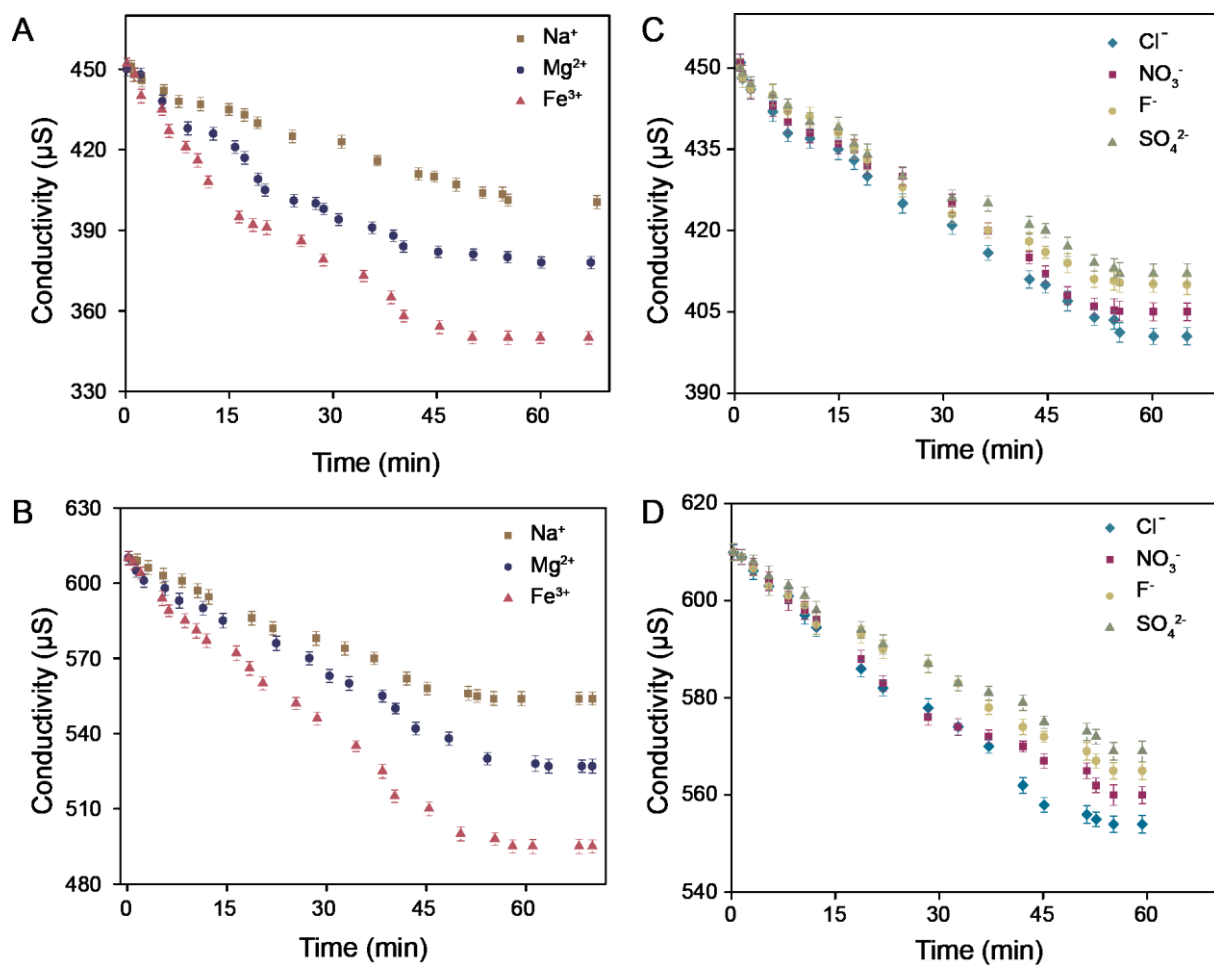


Figure S8. CDI performances of EAIERs electrodes using different cations (Na^+ , Mg^{2+} , and Fe^{3+}) with solutions of different conductivities: (A) 450 and (B) 610 μS . Similarly, anions (Cl^- , NO_3^- , F^- and SO_4^{2-}) with solution of different conductivities: (C) 450 and (D) 610 μS . The operating potential was maintained at 1.5 V during the measurements.

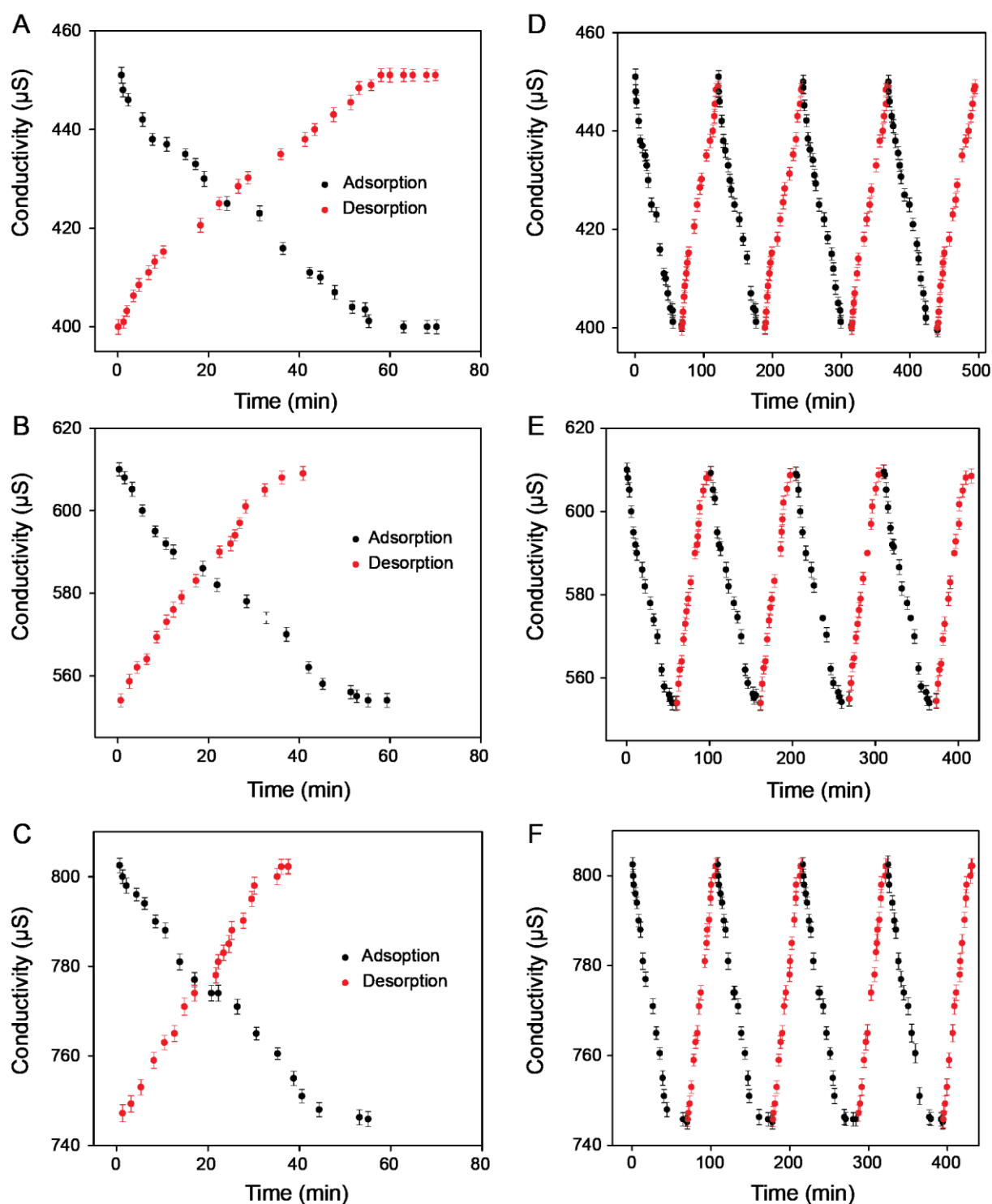


Figure S9. Adsorption capacities of covalently integrated EAIERs electrodes with NaCl solution of different conductivities: (A) 450, (B) 610 and (C) 802 μS , as a function of time at an applied voltage of ± 1.5 V. Desorption starts after the adsorption cycle was complete, at an applied potential of ± 1.5 V. Four adsorption-desorption cycles are shown in (D), (E) and (F).

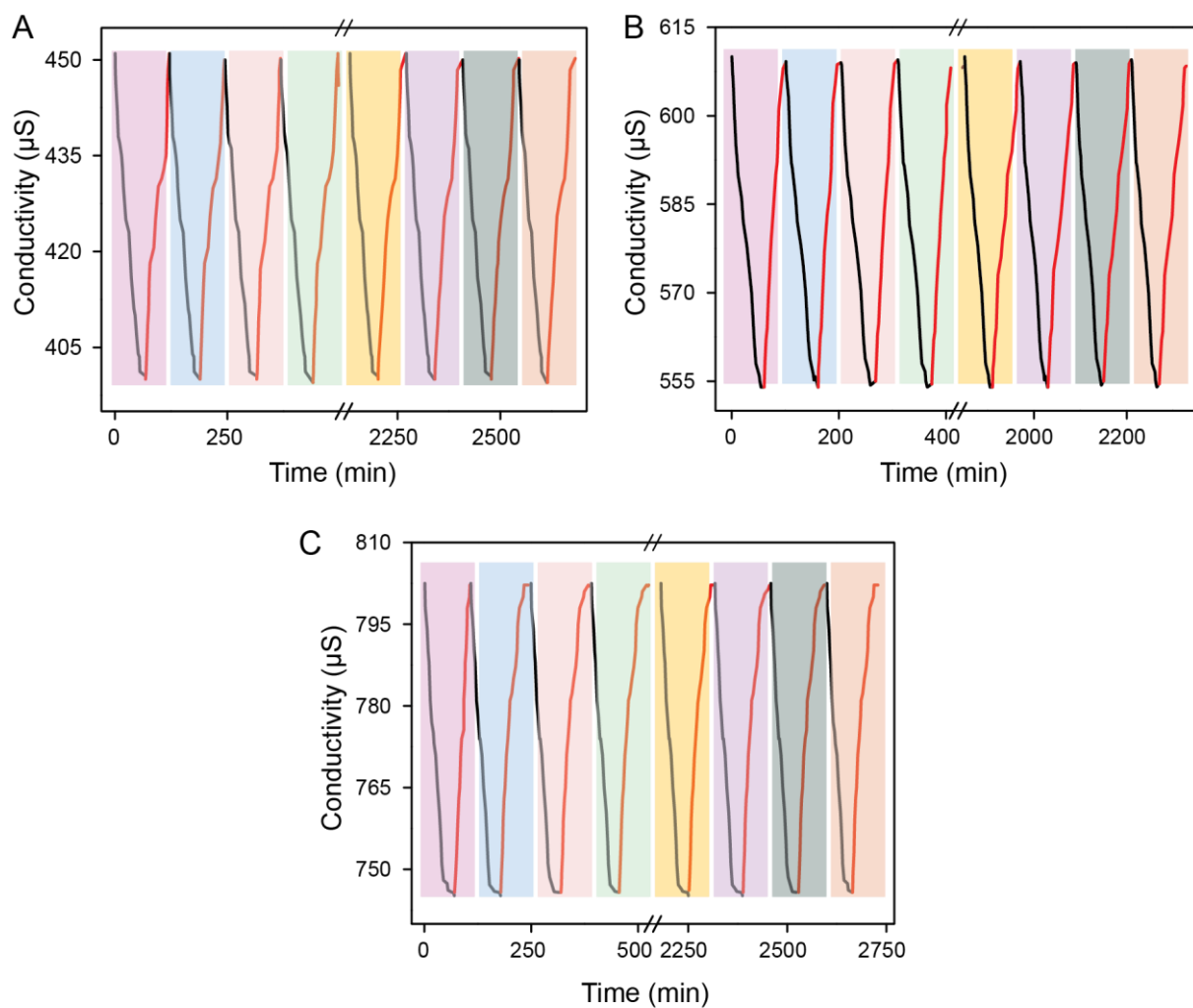


Figure S10. Electrode repeatability (20 cycles of adsorption-desorption) of a covalently integrated EAIERs electrode with different concentrations of NaCl solutions; (A) 450, (B) 610, and (C) 802 μS at an applied voltage of ± 1.5 V.

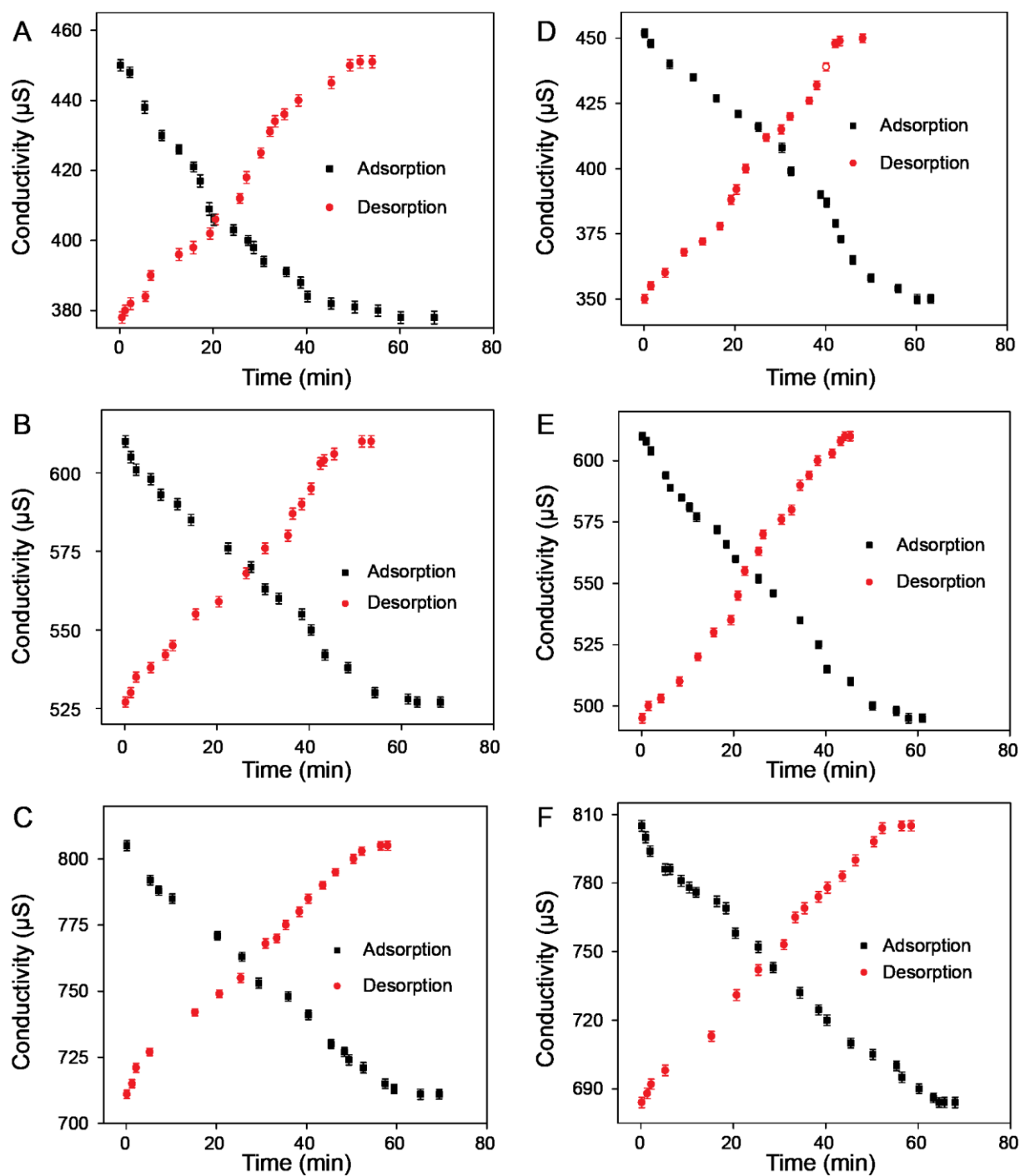


Figure S11. The adsorption and desorption rate of a covalently integrated EAIERs with MgCl_2 and FeCl_3 at different conductivities of 450 (A and D), 610 (B and E), and 802 μS (C and F) as at an applied voltage of ± 1.5 V.

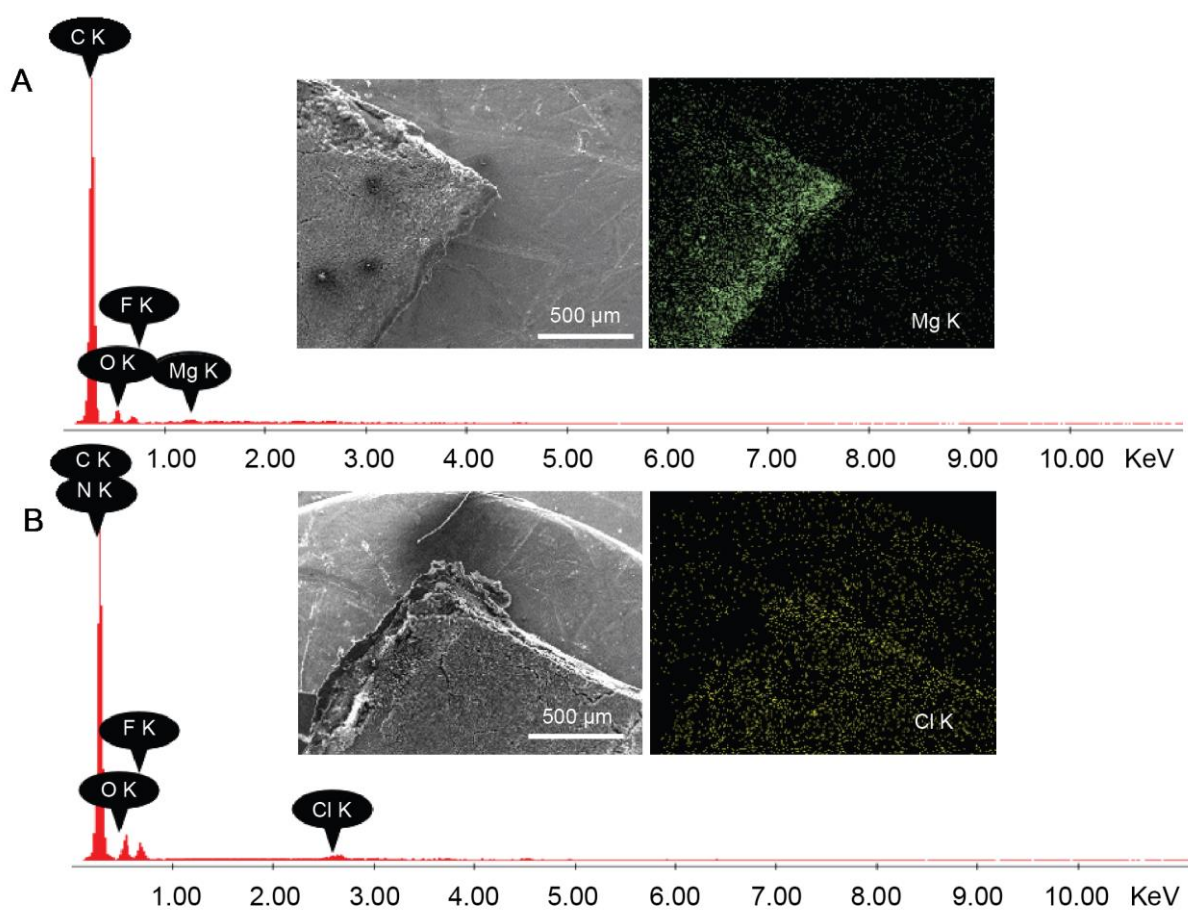


Figure S12. SEM EDS of MgCl_2 adsorption after single adsorption on (A) cathode and (B) anode. The corresponding SEM EDS and elemental mapping images are shown in the insets.

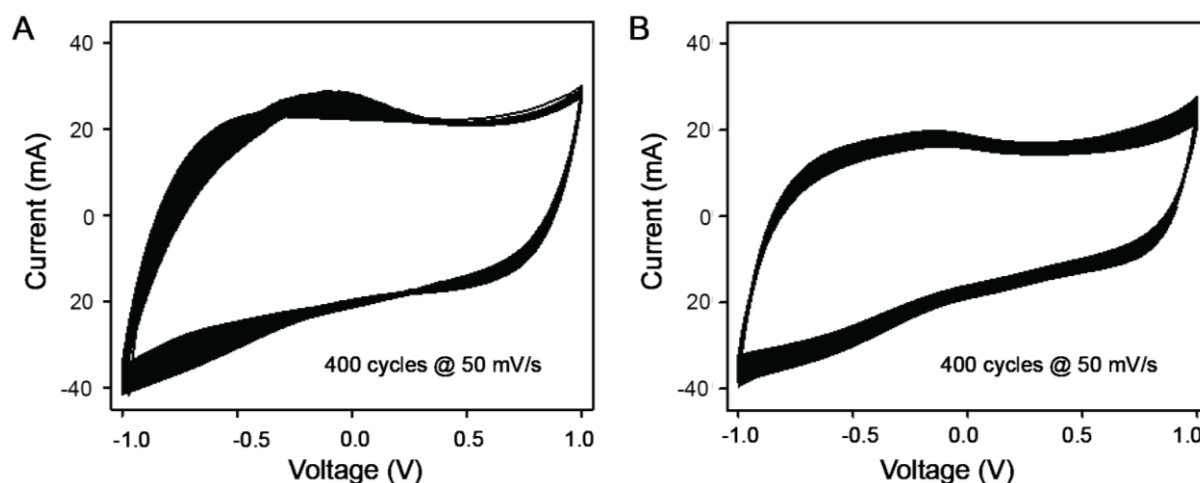


Figure S13. Cyclic voltammograms of (A) +ve and (B) -ve EAIERs electrodes and voltammetry was performed in 1 M NaCl at a fixed scan rate of 50 mV/s for 400 cycles.

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