**Supporting Information**

**How to achieve the optimal performance of capacitive deionization and inverted-capacitive deionization**

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This supporting information includes 3 figures.



**Figure S1.** (a) The constant-current charge curves of a three-electrode cell consisting an AC-coated working electrode, a PdHx reference electrode, and a Pt counter electrode in 8 mM NaCl for (1) cell, (2) Pt and (3) AC-coated working electrode, and (b) the corresponding conductivity against the AC electrode potential curve. The results were measured from *EOCP* to -0.7 V.

Clearly, from Figure S1b, the ionic conductivity of the testing solution regularly increases with the negative shift in the electrode potential of the AC-coated Ti electrode from *EOCP* (ca. 0.55 V) to -0.7 V vs. PdHx. Although the negative shift in the electrode potential of the AC-coated Ti electrode from *EOCP* to -0.7 V should reduce the conductivity of electrolyte because of ion removal from the electrolyte, the reactions on the Pt counter electrode change the ion concentration. Since the electrode potential of the Pt electrode rapidly reaches ca. 1.95 V during this test, the gradual increase in electrolyte conductivity is reasonably due to the significant oxygen evolution rate on the Pt counter electrode, leading to the generation of highly conductive protons. Hence, we cannot use the common three-electrode configuration to evaluate the ion-removal capability of electrode materials.



 **Figure S2.** The pH-time curves of (a) a cell consisting of two identical AC-coated Ti electrodes measured at a fixed cell voltage of (1) 0.8, (2) 1.2, (3) 1.6, and (4) 2.0 V in 8 mM NaCl for 60 min. (b) The pH-time curve of a charge-balanced cell measured at a fixed cell voltage of 2.0 V in 8 mM NaCl for 60 min.

From Figure S2a, the electrolyte pH gradually increases within the whole polarization period when the cell voltages are set at 0.8 and 1.2 V, especially for curve 2 measured at 1.2 V. This phenomenon has been attributed to the ORRs (O2 + 2H2O + 2e → H2O2 + 2OH− and/or O2 + 2H2O + 4e → 4OH−) on the negative electrode, generating OH−. The above reactions are unavoidable if the dissolved oxygen molecules in the electrolyte are not removed. On the other hand, the electrolyte pH initially increases and then monotonously decreases with the polarization time at cell voltages of 1.6 and 2.0 V. The decrease in pH indicates the generation of protons, reasonably attributed to the oxygen evolution on the positive electrode (i.e., 2H2O → O2 + 4H+ + 4e), because the positive electrode potential is located in the significant OER region. For the charge-balanced case in Figure S2b, pH gradually increases with the polarization time (because of the unavoidable ORRs) even though the cell voltage is set at 2.0 V. Hence, the charges applied to this charge-balanced cell are mainly employed for ion removal, indicating a higher efficiency in comparison with the charge-unbalanced cell.

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**Figure S3.** A scheme describes the CDI system employed in this work.