## **Supplementary Information**

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## SI-1: Measurement of the bed rise velocity in the optically accessible electrode compartment

As is seen in Fig. 3a, experiments in the optically accessible compartment always start with an empty compartment. Prior to the experiment, in the mixing vessel, we set a bead volume fraction of 10%, corresponding to 11.9 g of carbon beads and 200 g of 20 mM NaCl solution. When this suspension is pumped into the compartment from the bottom, first the compartment fills with electrolyte, then the beads enter and the fluidized bed will begin to form (Fig. 3b) and eventually fill the entire electrode compartment (Fig. 3c). The velocity of the fluidized bed can be calculated by

$$\frac{dx_{\rm bed}}{dt} = u_{\rm bed}$$
[S1]

where  $x_{bed}$  is the height of the growing bed, t is time, and  $u_{bed}$  is the bed velocity. In order to measure  $u_{bed}$ , we mark 2 cm increments along the height and record the time when the shock interface crosses each marking. The particle velocity used in Eq. 3,  $U_p$ , is calculated from the averaged  $u_{bed}$  over a 6 cm distance. At the end of the experiment, when the fluidized bed has completely filled the compartment, the flow direction is reversed until all the particles and water is flushed back into the mixing vessel (see Fig. 2). The experiment would then be repeated for a different pump flowrate (see *x*-axis of Figure 4b for the range of superficial velocities used).

# SI-2: Measurement of carbon skeleton density and bead porosity

The carbon "skeleton" density,  $\rho_c$ , was measured by placing a known mass of dry carbon beads,  $m_1$ , into a graduated cylinder, and then adding a known volume of deionized water,  $V_w$ . The cylinder was closed using parafilm, then the mixture was shaken, and after ~10 min (when outgas bubbles are no longer observed) the total volume, V, of the mixture is read off. From these measurements the carbon density was calculated using

$$\rho_{\rm c} = \frac{m_1}{V - V_{\rm w}}$$
[S2]

from which a value is obtained of  $\rho_c$ =1.7 g/mL which is near the typical value for activated carbons of  $\rho_c$ ~1.9 g/mL (Kim *et al.*, 2015).

In order to determine the porosity of the beads, p, we begin with a known mass,  $m_1$ , of dry beads in a beaker. Then, deionized water is added to the beaker, and the beaker is shaken until outgassing is no longer observed (the beads are water filled). We then empty the beaker onto a 75 micron sieve in order to collect the saturated beads, and to remove the water from between the beads. To remove surface water on the beads, we shake the sieve in order to distribute all beads over the sieve (single layer), and then use a wiper (Kimwipes, Kimberly-Clark) to absorb water from the bottom of the sieve mesh. This process is repeated after re-shaking the sieve, until the wiper remains dry. Subsequently, we measure the mass of the water-filled beads,  $m_2$ . The bead porosity, p, defined as the open bead volume divided by total bead volume, is calculated by

$$\frac{1}{p} = 1 + \frac{\rho}{\rho_{\rm c}} \frac{m_1}{m_2 - m_1}$$
[S3]

resulting in a number for bead porosity of p=0.67.

#### SI-3: Measurement of the bead volume fraction of the inflow into the electrode compartment

The bead volume fraction in Eq. 3,  $\phi_{bed}$ , requires knowledge of the bead volume fraction of the inflow into the electrode compartment,  $\phi_{in}$ , and thus we directly measure  $\phi_{in}$ . After the experiment described in section SI-1, the inlet tube leading to the cell is disconnected from the cell and maintained in the same orientation. We then flow the suspension for 2 min at a specified flowrate, and collect the outflow from the tube in a beaker and weigh it. Then the beaker is placed for 24 h into an oven at 105 °C and weighed again. From this, the mass of dry beads,  $m_1$ , and the total mass of water in the suspension,  $m_w$ , is obtained. This experiment was repeated for several flow rates within the range tested in SI-1, but the measured  $\phi_{in}$  did not vary significantly with flow rate. The parameter  $\phi_{in}$  is obtained using

$$\frac{m_{\rm 1}}{\rho_{\rm c}(1-\rho)} = \phi_{\rm in} \cdot \left(\frac{m_{\rm w}}{\rho} + \frac{m_{\rm 1}}{\rho_{\rm c}}\right)$$
[S4]

resulting in a number for inflow bead volume fraction of  $\phi_{in}$ ~5 vol%.

## SI-4: Fitting experimental results to the Richardson-Zaki equation

In Figure 4, we plotted the electrode CWP versus electrode superficial velocity, and fit this to theory. Here, we plot the same data, but in the form of the experimentally measured bed voidage,  $1-\phi_{bed}$ , versus the relative velocity  $U_p-U_w$ , in order to fit the data to the Richardson-Zaki equation (Eq. 2). While  $U_p$  was obtained by measuring the kinematic shock velocity,  $U_w$  was calculated from a volume conservation applied to the compartment,



$$U_{\rm sup} = \phi_{\rm bed} U_{\rm p} + (1 - \phi_{\rm bed}) U_{\rm w}$$
 [S5]

**Figure SI-1**: A plot of the measured relative velocity,  $U_p - U_w$  versus measured bed voidage for various electrode thicknesses, fitted to the Richardson-Zaki equation (blue curve).

We fit the experimental data shown in Fig. SI-1 to Eq. 2, using the exponent *n* and the parameter  $U_T$  as fitting parameters. The results of this fitting is shown in SI-1 (blue curve), and we find a best fit parameters of n = 1.1, and  $U_T = 2.5$  mm/s. This value of *n* deviates significantly from n=4.65, the value expected for ideal sedimentation with creeping flow about smooth, spherical beads. However, our experiments deviate significantly from this ideal case, as we likely have significant entrance and wall effects in our electrode compartment, our beads are non-smooth and highly porous, and volume fractions are very high (Eq. 2 was originally derived for more dilute settling suspensions) (Richardson & Zaki, 1997; Biesheuvel *et al.*, 2001). Further, we note our experiments deviate from creeping flow, as we calculate the Reynolds number based on the bead diameter to be in the range Re = 1-5. Future work will investigate these effects, to understand their impact on bed CWP and cell performance. We also compare fitted  $U_T$  value to the known analytical solution for the terminal velocity of a sphere in creeping flow (Probstein, 2005),

$$U_{\rm T} = \frac{2}{9} \frac{a^2}{v} g \left( \frac{\rho_{\rm p}}{\rho} - 1 \right)$$
 [S6]

where using a sphere radius of  $a=75 \mu$ m, and the density of a water-filled bead of  $\rho_p = 1.23$  g/mL, we obtain a value of  $U_T = 3.17$  mm/s, which is very near to the extracted value of  $U_T$  from our model-to-data fitting of  $U_T = 2.5$  mm/s.

#### SI-5: Mass balance theory

The dashed red line in Figure 5 is plotted from the results of a salt mass balance calculation, which we describe here. For the feed channel in the Fbed CDI cell, several minutes after applying the voltage, the effluent concentration is roughly constant at about 11.5 mM, see Figure 5. Multiplying the reduction in salt concentration of the feedstream (~ 8.5 mM), with the volume flow through the feedwater channel, a salt removal rate (in mol/s),  $\Phi_{salt}$ , can be calculated. We set up an unsteady electrode mass balance given by

$$V_{\text{elec}} \frac{\partial \boldsymbol{c}_{\text{salt,elec}}}{\partial t} = \Phi_{\text{salt}} + \Phi_{\text{vol,mv}} (\boldsymbol{c}_{\text{salt,elec,in}} - \boldsymbol{c}_{\text{salt,elec}})$$
[S7]

where  $V_{\text{elec}}$  is the total volume of electrolyte used in the electrodes including in the cell, tubing and mixing vessel,  $c_{\text{salt,elec}}$  is the salt concentration in this recycle volume,  $\Phi_{\text{vol,mv}}$  is the volume flow rate of feedwater to the mixing vessel, and  $c_{\text{salt,elec,in}}$  is the salt concentration of the feedwater. Eq. [S7] can be integrated to describe  $c_{\text{salt,elec}}$  as function of time, using the inflow salinity in the electrode (the same as that into the feedwater channel) of  $c_{\text{salt,elec,in}} = 20$  mM and the volume of feedwater pumped to the mixing vessel,  $\Phi_{\text{vol,mv}}$ , being 23% of the total inflow into the system (where system inflow includes 0.15 mL/min to the vessel and 0.5 mL/min to the cell feed channel). To obtain a fit, a value for the recycle volume is used of  $V_{\text{elec}}$ =185 mL, about 8% below the starting solution volume of  $V_{\text{elec,exp}}$ =200 mL. A slighly reduced value for  $V_{\text{elec}}$  is needed likely due to the the loss in volume when initially closing the mixing vessel after filling, as during this step we observed that some water flows into the thin tube and spills over into the overflow compartment. The calculated results of  $c_{\text{salt,elec}}$  are shown as the red dashed line in Fig. 5.

#### SI-6: Current, concentration, and current efficiency measurements of the Fbed CDI cell

For the long-term experiment shown in Fig. 5, we here in Fig. S1 show the current response of the experimental cell after application of the cell voltage. The inset shows the early time current response. In Figs. S2a and S2b, we show the current response and cell effluent concentration for eight different experimental conditions (four different cell voltages and two different feed flowrates). The data from Figs. S2a and S2b are used to calculate the current efficiency, shown in Fig. S3. Current efficiency is defined as the molar flux of salt removed from the feedwater divided by the molar flux of electrons transferred between electrodes by the external power supply, and is a widely used metric to quantify the energy efficiency of FCDI and electrodialysis cells. Here, we vary the feed flow rate and cell voltage applied, and report the resulting current efficiency for the 500 s period after the initial strong transient seen in cell current (see Fig. S2a) and feed concentration (see Fig. S2b). From the results in Fig. S3, we see that varying feed flow rate does not appreciably affect the measured current efficiency. However, a clear trend emerges with increasing cell voltage, as the current efficiency,  $\lambda$ , decreases with increasing cell voltage,  $V_{cell}$ , from a near unity efficiency at  $V_{cell}$ =1.0 V to about  $\lambda$ =0.9 at  $V_{cell}$ =1.9 V. The latter trend is likely due to the increasing prevalence of side reactions at higher cell voltages, which leads to an increasing fraction of the total current not used to electrosorb ions.

We also note at longer Fbed CDI run times, for example, from the experiment of Fig. 5, current efficiency slowly decreases. From the data in Figs. 5 and S1, we see that current efficiency reaches roughly 85% after 4 days. We hypothesize that this may be due to the slowly increasing salt concentration in the electrode compartment (and so in the electrode itself) over the long-term experiment, which may result in a diffusion-driven backflux of salt into the feed channel. We note that this effect can also be caused by changes to the carbon beads (either physical or chemical) over the experiment. Future work will delve into degradation mechanisms affecting the Fbed CDI cell.



Figure S1: Current response of the Fbed CDI cell during the experiment reported in Fig. 5.



**Figure S2**: a) Current response of the Fbed CDI cell for eight different experimental conditions. These conditions include cell voltages of  $V_{cell}$ =1, 1.3, 1.6 and 1.9 V, and feed channel flow rates of  $\Phi$ =0.5 and 1.5 mL/min. b) Feedwater effluent concentration from the charging Fbed CDI cell for the same eight experimental conditions shown in a).



**Figure S3**: Measured Fbed CDI current efficiency versus cell voltage, for different feed flow rates (using the data shown in Fig. S2). Efficiencies are near-unity at low voltages ( $V_{cell}$ =1.0 V), and decrease with increasing cell voltage likely due to the effect of parasitic side-reactions.

# References

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