## Supporting Information

## Effects and Controls of Capacitive Hysteresis in Ionic Liquid Electrochemical Measurements

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Time (minutes)

Figure S1. Schematic illustration of the three different data acquisition protocols used in this study. HoldE: Hold potential. OCP: Open Circuit Potential rest. NoEq: No equilibration time. Each EIS spectrum in the present study takes ca. 2.5 min to acquire.



Figure S2. (a) Scan rate dependent DC CVs for the medium 2.1 V potential range at 800, 500, 300, 100, 50, and 20 mV s<sup>-1</sup>. The inset shows the 20 mV s<sup>-1</sup> CV with no evidence of peaks in the DC voltammogram. The arrow points to increasing scan rates. (b) Overlay of representative DC voltammograms at 100 mV s<sup>-1</sup> for the large (3.1 V), medium (2.1 V), and small (1.1 V) potential ranges examined.

The electrochemical equivalent circuit used to model EIS data consists of a bulk electrolyte resistance  $(R_s)$  in series with a parallel-connected high frequency capacitance  $(C_{hf})$  and a constant phase element (CPE) as shown in Figure 2a. CPEcontaining equivalent circuits have been discussed controversially in the IL literature,<sup>S1-S7</sup> with the main criticism arising from the physical interpretation of a CPE, which is often used as a 'universal' fit parameter. Ohmic corrected modulus and phase angle plots (see **Figure S3a**) subtract out the bulk property (i.e.  $R_{o}$ ) from the Z' values, which permits the identification of CPE characteristics to be seen if present. At frequencies <10 kHz the slope of the modulus is -0.9 (where -1 represents ideal CPE behavior) approximately the negative of the  $\alpha$  value (0.91) from the fitting process. The phase angle plot suggests a value of -81° (where -90° represents ideal CPE behavior) at frequencies <10 kHz. The  $\theta_{adj}$  term is related to the  $\alpha$  value from the fitting process by  $\alpha = -\theta_{adj}/90^\circ = 0.90$ , in excellent agreement with the value from the modulus slope. Orazem et al. demonstrated there can be geometry induced frequency dispersion of impedance data above a characteristic frequency  $(f_c)$ .<sup>S8</sup> For the present electrochemical system (using  $\kappa = 0.0022 \ \Omega^{-1} \ \text{cm}^{-1}$ , <sup>S9</sup>  $Q = 1.97 \times 10^{-6} \ \text{s}^{\alpha} \ \Omega^{-1} \ \text{cm}^{-2}$ ,  $\alpha =$ 0.91 and  $r_0 = 0.15$  cm) we find that  $f_c > 3$  kHz, which is in qualitative agreement with Figure S3a (see vertical red dash-dot line). Lastly, the residual error of the modulus and the phase angle for the representative data set at 0.0 V vs. Fc/Fc<sup>+</sup> is shown in Figure S3b and demonstrates that the difference between the measured and calculated data is less than 2 % and 2° (omitting the four highest frequencies) for the modulus and phase angle, respectively.

It should be noted that the average resistance value from this work is ca. 920 ± 50  $\Omega$ . The time constant is calculated from the average  $R_s$  and  $C_{\text{eff,surf}}$  values to be on the order of 1 ms.



Figure S3. (a) Ohmic corrected modulus (grey squares) and phase angle (purple upward triangles) Bode plots from representative 0.0 V vs. Fc/Fc<sup>+</sup> EIS data set. At frequencies <10 kHz the plots reveal CPE behavior. The dashed black line (----) denotes -81° for the phase angle and the red dash-dot line (----) corresponds to the characteristic frequency ( $f_c$ ) above which the electrode geometry can influence our impedance data. (b) Residual error plots of the modulus and phase angle for the 0.0 V vs. Fc/Fc<sup>+</sup> EIS data set. The arrows point to their respective axis.



Figure S4. Zoomed in capacitance-potential curves from the three different potential windows (a) large = 3.1 V, (b) medium = 2.1 V, and (c) small = 1.1 V. The anodic and cathodic potential scan directions are denoted with filled and open symbols, respectively.



Figure S5. Capacitance-potential curves from the three different data acquisition protocols showing (a) anodic and (b) cathodic scan directions. HoldE = hold at potential for 10 min, OCP = cell left at OCP for 10 min, and NoEq = data acquired with no wait time in-between collecting EIS spectra.



Figure S6. Capacitance-potential curves obtained from three different data acquisition protocols for single-frequency impedance (10 Hz, 10 mV rms) measurements showing (a) anodic and (b) cathodic scan directions. b2b = back-to-back acquisition, OCP = cell left at OCP for 10 min before switching scan direction, and HoldE = held at switching potential for 10 min before changing scan direction.

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