Electrochemistry

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Formulation of Ionic-Liquid Electrolyte To Expand the Voltage Window of Supercapacitors**

Katherine L. Van Aken, Majid Beidaghi, and Yury Gogotsi*

Abstract: *An effective method to expand the operating potential window (OPW) of electrochemical capacitors based on formulating the ionic-liquid (IL) electrolytes is reported. Using model electrochemical cells based on two identical onion-like carbon (OLC) electrodes and two different IL electrolytes and their mixtures, it was shown that the asymmetric behavior of the electrolyte cation and anion toward the two electrodes limits the OPW of the cell and therefore its energy density. Also, a general solution to this problem is proposed by formulating the IL electrolyte mixtures to balance the capacitance of electrodes in a symmetric supercapacitor.*

While known for their high-power performance compared to batteries, electrochemical double layer capacitors (EDLCs) need an increase in energy density to expand their applications. EDLCs store charge using electrostatic attraction of electrolyte ions to the surface of a charged electrode.[1] The energy density of an EDLC device is proportional to its capacity and also the square of its operating potential window (OPW) according to Equation (1),

$$E=\frac{1}{2}CV^2 \qquad (1)$$

where C is the capacitance of the device and V is the OPW.[1] Accordingly, the energy density of an EDLC can be increased by either achieving higher electrode capacity or by expanding the OPW of the device. Increasing the capacity of the EDLC electrodes by modifying carbon materials has been explored as a path to improving their energy density.[2–4] However, according to Equation (1), increasing the OPW, which mostly depends on the stability of the electrolyte, has a much larger impact on the energy density of the device.[5] Therefore, to achieve higher-energy densities, electrolytes based on organic solvents or ILs are preferred over aqueous electrolytes because of their wider OPW.[6] However, when a symmetric supercapacitor is assembled with these electrolytes, the maximum OPW of the device is always lower than the expected voltage stability window of these electrolytes. This is especially notable for IL electrolytes, which are stable in the 5–6 V window when Pt electrodes are used,[3] but rarely work beyond 3.5 V in supercapacitors. One of the main reasons for the smaller working potentials is the parasitic reactions in the cell because of impurities of the electrode material and also surface functional groups.[7] The OPW of an EDLC can also be affected when the working potential ranges of the negative and positive electrodes are asymmetric. This can happen if the potential of zero voltage (E_{0V})[8] of the electrodes is not in the middle of the electrolyte stability window and/or when the capacities of the symmetric electrodes are different for positive or negative electrolyte ions.[9] During the operation of an EDLC, the charge (Q) on the positive and negative electrodes should be balanced.[10] Since $Q=CV$, if the capacity of the positive (negative) electrode is lower than that of the negative (positive) electrode, the positive (negative) electrode will compensate by operating at a higher potential window to balance the charge on the two electrodes. This creates an uneven distribution of the total window across the two electrodes. If the larger potential window of the two reaches the stability limit, the whole cell will exhibit electrolyte decomposition characteristics similar to operating a cell at a potential above its stability window. There are currently a few reported methods for correcting the asymmetric OPWs of the two electrodes, including balancing the electrode masses,[11,12] choosing two different electrode materials,[13] and injecting charge into one or both electrodes before testing.[8] By all three methods, the E_{0V} of the cell is forced to land in the middle of the potential stability window of the electrolyte, creating equal OPWs for both electrodes.[9,14] As a result, the working potential range of the device can be extended closer to the maximum voltage window allowed by the electrolyte. However, there are a few problems associated with each of these methods as explained further in the Supporting Information. For instance, mass balancing, which is currently the preferred method in commercial cells, equalizes the OPW of the electrodes but has a negative effect on the specific capacitance of the cell because of the additional mass in one of the electrodes. We propose an alternative and a much simpler method: formulation of the electrolyte to balance the OPW of the two electrodes in a symmetric device. Using a model electrode/electrolyte system, we have studied the effect of the asymmetric performance of the electrolyte cations and anions on the overall OPW of the cell, and suggested a method to balance the OPW of the cell and increase its energy density.

Our model system consists of onion-like carbon (OLC)[15] electrodes and two commercially available IL electrolytes, pure or mixed in different ratios. OLC has an open surface

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[*] K. L. Van Aken,[+] Dr. M. Beidaghi,[+] Prof. Y. Gogotsi
A. J. Drexel Nanomaterials Institute and
Department of Materials Science and Engineering
Drexel University, Philadelphia, PA 19104 (USA)
E-mail: gogotsi@drexel.edu

[+] These authors contributed equally to this work.

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structure which is free from micropores. By using OLC, we eliminate the effect of pore size relative to electrolyte ion size on the capacitance of the electrodes[15–18] and also eliminate transport limitations in a microporous carbon network.[16,19] Symmetric cells were first assembled using two identical OLC electrodes and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI)[20] as the electrolyte. By applying a testing method that is further explained in the Supporting Information, we monitored the cyclic voltammetry (CV) response of the full cell and the individual electrodes at potential windows of 2.5, 3, and 3.5 V. Figure 1a shows the CV results for a 2.5 V voltage window plotted for the full device (black) as well as the individual electrodes (negative electrode in red and positive electrode in blue). To make the comparison of the cyclic voltammograms easier, this plot was modified by flipping the direction of the y axis for the negative electrode. When the OPW was set to 2.5 V (Figure 1b), a typical butterfly shape for the cyclic voltammogram was observed with no sign of electrolyte decomposition or any side reactions. As shown in Figure 1c, when the voltage is increased to 3.0 V, there is a slight evidence of electrolyte decomposition with a sudden increase of the current near the low- and high-potential limits and the appearance of a small hump in the middle of the potential range. At a wider OPW of 3.5 V, definite reaction peaks confirm electrolyte decomposition (Figure 1d). From these experiments, we can conclude that the maximum OPW for EMI-TFSI electrolyte is less than 3.0 V. The identical electrodes show different responses toward the anion and cation of the electrolyte, as the working (positive) electrode operates at a wider potential window compared to the counter electrode resulting in an asymmetric shape of cyclic voltammograms for the two electrodes. Since the electrodes are identical, the different behavior of negative and positive electrodes is clearly a result of the different interactions (double layer structure) that the two electrodes have with the different ions. Therefore, we can conclude the asymmetric performance and resulting limited OPW is related to the different electrolyte ions. Increasing asymmetry with the scan rate suggests that differences in ion mobility may be responsible for this behavior, but other factors such as the size and shape of the ions and their interactions with carbon surfaces may affect the symmetry as well (see Figure S2a in the Supporting Information).

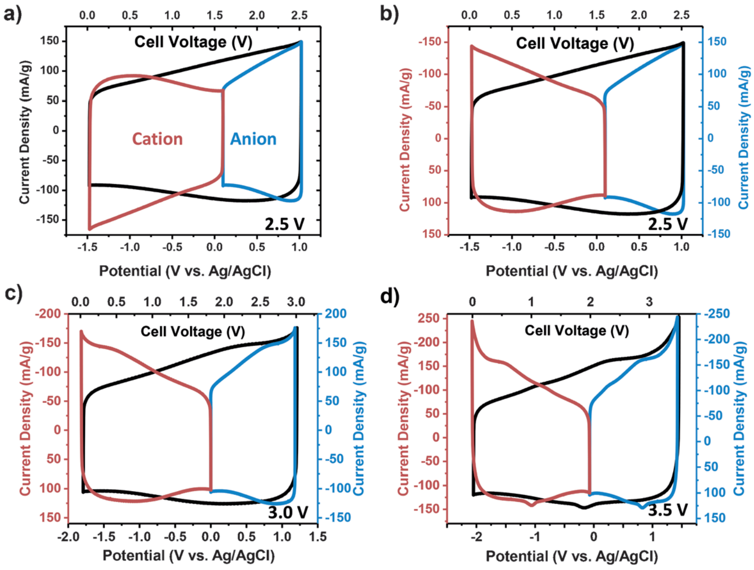

Figure 1. Cyclic voltammograms for cells assembled with EMI-TFSI electrolyte showing the response of the whole cell (black line) and also individual electrodes. a) A standard plot at OPW of 2.5 V, b) same as (a) with the reverse current (*y*) axis for better visual comparison of cation and anion response. CV responses are also plotted for OPWs of c) 3.0 V and d) 3.5 V. All CV scan rates are 10 mV s^{-1}.

To confirm the relation of this behavior to properties of the electrolyte, we repeated the experiment with another commercially available IL, namely EMI-BF$_4$, as well as different mixtures of the two electrolytes. The cations are the same in the two electrolytes (EMI) and the two anions are very different in their size, shape, and in their constituent components (Figure 2g–i). The two electrolytes were mixed by adding EMI-BF$_4$ to EMI-TFSI at 10, 20, 50, and 80 vol%. Figure 2 shows the CV curves at different scan rates for pure electrolytes and the mixtures. In all six plots, the cyclic voltammograms for 5, 10, and 20 mV s^{-1} at a cell voltage of 2.5 V are shown for the individual electrodes. The asymmetry for pure EMI-TFSI can be seen in Figure 2a, where the negative electrode (red) operates at a higher potential than the positive electrode (blue) for all CV scan rates. As discussed above, this suggests that the cation-negative electrode combination results in less charge, requiring the electrode to compensate with a higher potential. Figure 2f shows the same results for pure EMI-BF$_4$, where the same trend of a higher negative electrode potential is evident. The different IL mixtures are shown in Figure 2b–e where the plots are presented with increasing concentration of EMI-BF$_4$. A few interesting observations can be made from these CV results. Figure 2d shows the CV curves for the case of the electrolyte with 50% EMI-BF$_4$ and the plot appears to be similar to the CV of pure EMI-TFSI in terms of negative and positive electrode symmetry, where the negative electrode operates at the higher potential. Conversely, cyclic voltammograms for the case of the electrolyte with 80% EMI-BF$_4$ (Figure 2e) show the opposite effect, suggesting that for this electrolyte, the negative electrode operates at a lower potential than the positive electrode. Finally, the CV curves for the other two electrolytes with 10% EMI-BF$_4$ (Figure 2b) and 20% EMI-BF$_4$ (Figure 2c) visually appear to be the most symmetric of all the mixtures, with the 20% being the best overall. This suggests that by adding a small amount of the new anion to the original one, we were able to change the resulting symmetry of the two electrodes of the device. A quantitative analysis of the symmetry of the cyclic voltammograms for the different electrolyte mixtures is shown in Figure S2a, where the ratio of the positive electrode potential over the negative electrode potential is plotted versus the CV scan rates for all concentrations. This plot also confirms that the electrolyte

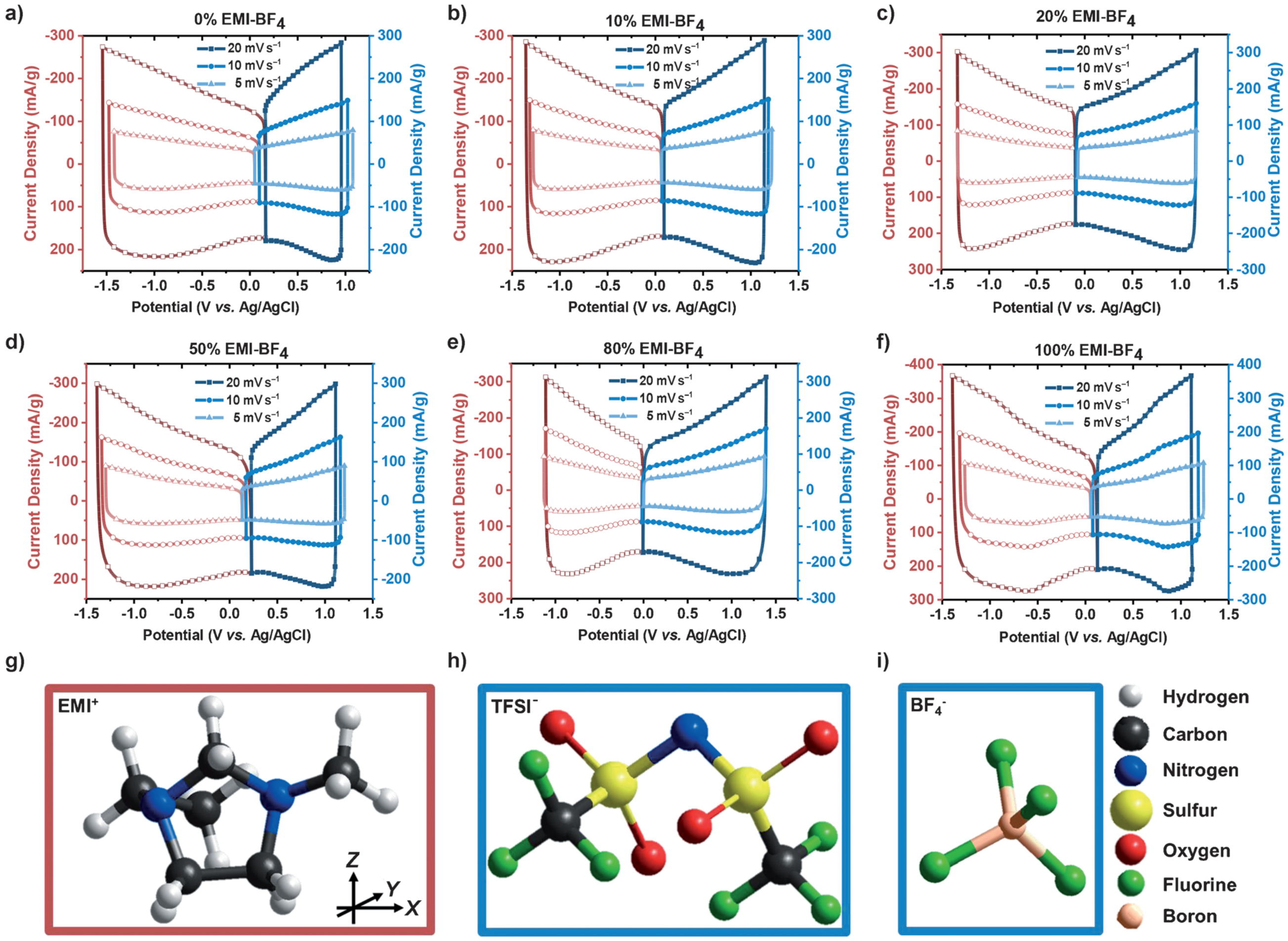

Figure 2. Cyclic voltammograms for cells assembled with mixtures of EMI-TFSI and EMI-BF_4 with different volumetric percentages of EMI-BF_4, including a) 0%, b) 10%, c) 20%, d) 50%, e) 80%, and f) 100%. Operating potential window in all cases is 2.5 V and three scan rates are shown (5, 10, and 20 mVs^{-1}). Models of ions contained in the ionic-liquid electrolytes used in this study, including g) EMI^+, h) $TFSI^-$, and i) BF_4^-.

mixture with 20% EMI-BF_4 has a negative to positive electrode potential ratio closest to 1, especially at low scan rates.

To confirm that the symmetric working potentials of the positive and negative electrodes will result in a higher OPW of the device, cyclic lifetime tests were performed at an elevated working potential of 3.5 V on symmetric cells assembled using the two pure electrolytes and the best performing mixed electrolyte (20% EMI-BF_4). The charge and discharge tests were performed for 10000 cycles and the capacitance and resistance of the cells were calculated for each cycle and shown in Figure 3a,b, respectively. Both figures show that 3.5 V is beyond the stability window for EMI-TFSI since after 10000 cycles the cell that uses this electrolyte retains only 20% of its initial capacitance with almost six-fold increase in resistance. The device using the pure EMI-BF_4 electrolyte performs much better as it retains 80% of its capacitance, reaching its cycle life limit, and shows a two-fold increase in resistance. Finally, the cell assembled with the IL mixture containing 20% EMI-BF_4 performs the best, retaining more than 95% of its capacitance and showing a very small increase in resistance of about 1 $\Omega\,cm^{-2}$. These tests show that an OPW of 3.5 V is much larger than the stability window of EMI-TFSI electrolyte, but when 20% of EMI-BF_4 is added, the cell can operate at this wider voltage window for a much longer time. As explained before, the main reason for this behavior is the symmetry of the OPWs of the two electrodes, which is a result of balancing the amount of charge stored by the electrodes. The behavior of the cells with different electrolytes was also compared using impedance spectroscopy[21] and the results are shown in Figure 3c. The solid lines show the Nyquist plots of the cells before cycling, noticeably the same for all three electrolytes. While the shape of the plot for the 20% mixture remains the same, aside from slight increase in resistance shown by increase in the x intercept of the plot, the other two plots exhibit changes confirming electrolyte degradation. For the cell with EMI-TFSI as the electrolyte, the appearance of a larger semicircle at high frequencies after the cycling tests indicates an increase in interfacial resistance of the cell because of electrolyte degradation. The cell with EMI-BF_4 as the electrolyte also shows an increase in the size of the semicircle. These results confirm that the IL mixture is more stable at high OPWs compared to the individual ILs.

By mixing the two pure ILs, a new electrolyte is created that shows properties different from its constituents.[22] The electrochemical studies in this work show that the cations and

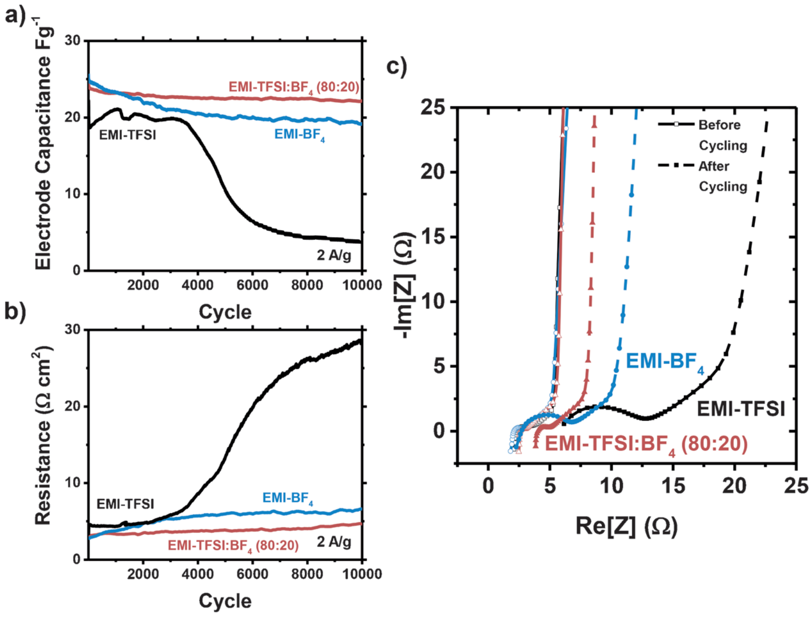

Figure 3. Cyclic performance over 10000 cycles for cells assembled with EMI-TFSI, EMI-BF$_4$, and the 20% EMI-BF$_4$ mixture, showing a) electrode capacitance and b) resistance changes during cycling. c) Nyquist plots for all cells before (solid lines) and after cycling (dashed lines).

anions of the pure IL electrolytes exhibit different behaviors when used in a symmetric supercapacitor. This can be attributed to the different size, molecular weight or diffusion coefficient of the ions in the electrolyte. One of the important consequences of this different behavior of ions, as was shown in this study, is the asymmetric charge storage in the two identical electrodes of a symmetric supercapacitor, which results in a lower OPW of the cell, limiting the energy density. Here we showed, for the first time, that by using an IL mixture, a balanced charge storage can be achieved in the cell and the OPW of the supercapacitor can be increased. This finding opens a door for further improvement of the energy density of supercapacitors. While we have focused on a model system of OLC electrodes and IL electrolytes, the method described in this study can potentially be used for other electrode/electrolyte systems. However, when using porous carbon electrodes, the effect of pore size on adsorption of different ions should be considered. Also, when using organic or aqueous electrolytes the effect of ion solvation shells should be taken into account.[20]

Keywords: electrochemical capacitor · electrochemistry · energy density · ionic liquids · operating potential window

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