Double layer capacitance of ionic liquids for electrolyte gating of ZnO thin film transistors and effect of gate electrode.


Supplementary Information

Analysis of the electrochemical impedance spectroscopy (EIS)

The Warburg impedance element represents the contribution to the impedance of semi-infinite diffusion mechanism to/from a flat electrode. It contributes equally to the real and imaginary parts of impedance i.e.:

\[ Z_W = \frac{A_W}{\omega^{0.5}}(1 - j) \]  

where \( \omega \) is the angular frequency of the AC voltage signal, \( j \) is the imaginary unit, \( A_W \) the Warburg coefficient, depending on diffusion coefficient of ionic species, \( D \), and their surface concentration.

The Constant Phase Element (CPE) is used to represent the response of non-ideal and non-homogeneous systems\(^1\). The expression for such an impedance is given by:

\[ Z_{CPE} = \frac{1}{Q(j\omega)^n} \]  

(2)

Depending on the value of \( n \) (ranging from -1 to 1) this element may in turn represent a non ideal capacitor, an inhomogeneous resistance or either an inhomogeneous diffusion mechanism. If \( n=1 \) the CPE becomes an ideal capacitor, i.e. \( Q = C \). Similarly, if \( n = 0 \) then \( Q = 1/R \) (being \( R \) an ideal resistance), or with \( n=0.5 \) the \( Z_{CPE} \) reduces to the ideal Warburg diffusion impedance.

For comparison purposes a capacitance \( C(\omega) \) can be calculated from \( Z_{CPE} \) provided that \( n \approx 1 \). Under such a condition the following equivalence holds:
\[ |Z_{\text{CPE}}| = \frac{1}{Q \omega^n} = \frac{1}{C(\omega)\omega^n} \]

(3)

where \( |Z_{\text{CPE}}| \) being the modulus of \( Z_{\text{CPE}} \), one can write:

\[ C(\omega) = Q \omega^{n-1} \]

(4)

The impedance of the Warburg Short (\( W_s \)) diffusion element can be written as

\[ Z_w = \frac{W_{sr}}{\omega^{0.5}}(1 - j) \text{tanh}(W_{sc}(j\omega)^{0.5}) \]

(5)

and represents a finite-length diffusion mechanism with transmissive boundary\(^2\).

\( W_{sr} \) is equal to Warburg coefficient and \( W_{sc} = d/D^{0.5} \), where \( d \) is the Nernst diffusion layer thickness.

Table S1 shows the impedance parameters obtained after fitting the data with the two equivalent circuit models presented in the manuscript.

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<thead>
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<th>[\text{bmim][PF}_6]</th>
<th>[\text{bmim][BF}_4]</th>
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<tbody>
<tr>
<td><strong>Fitted parameters</strong></td>
<td><strong>At 0V</strong></td>
<td><strong>At -1.5V</strong></td>
</tr>
<tr>
<td>(R1)(ohm)</td>
<td>333.7</td>
<td>191.1</td>
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<tr>
<td>(R2)(ohm)</td>
<td>(4.3 \times 10^5)</td>
<td>(4.04 \times 10^5)</td>
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<tr>
<td>(CPE1)</td>
<td>(1.2 \times 10^{-7})</td>
<td>(3.8 \times 10^{-7})</td>
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<tr>
<td>(CPE2)</td>
<td>(1.7 \times 10^{-7})</td>
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<tr>
<td>(Ws)(ohm)</td>
<td>(\text{--------})</td>
<td>(4.7 \times 10^5)</td>
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<tr>
<td>(n1)</td>
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<td>0.9</td>
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<tr>
<td>(n2)</td>
<td>0.7</td>
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References