



*Supplementary materials*

# ***In situ* X-ray photoelectron spectroscopic and electrochemical studies of the bromide anions dissolved 1-ethyl-3-methylimidazolium tetrafluoroborate**

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**Table S1.** C 1s, N 1s, B 1s, F 1s and Br 3d PE binding energies (eV) measured by *in situ* XPS for 5 wt% EMImBr + EMImBF<sub>4</sub> | C(Mo<sub>2</sub>C) system polarized at various negative potentials (corresponding spectra are shown in Figures. 2a – e).

	$E = -0.27 \text{ V}$	$E = -1.27 \text{ V}$	$E = -2.07 \text{ V}$
C 1s			
C1	287.6(0)	288.4(0)	288.7(0)
C2 + C3	286.9(0)	287.7(0)	288.0(0)
C4 + C6	286.4(0)	287.2(0)	287.5(0)
C5	285.3(5)	286.1(5)	286.6(5)
N 1s	$E = -0.27 \text{ V}$	$E = -1.27 \text{ V}$	$E = -2.07 \text{ V}$
N1	402.2(0)	402.9(5)	403.5(5)
N2	—	400.4(5)	400.9(0)
B 1s	$E = -0.27 \text{ V}$	$E = -1.17 \text{ V}$	$E = -2.07 \text{ V}$
B1	194.0(0)	194.8(0)	195.2(5)
B2	—	193.3(5)	193.9(5)
F 1s	$E = -0.27 \text{ V}$	$E = -1.17 \text{ V}$	$E = -2.07 \text{ V}$
F	686.8(0)	687.9(0)	688.2(5)
Br 3d	$E = -0.27 \text{ V}$	$E = -1.17 \text{ V}$	$E = -2.07 \text{ V}$
Br 3d <sub>5/2</sub>	67.3(0)	68.0(5)	68.5(5)
Br 3d <sub>3/2</sub>	68.3(0)	69.1(0)	69.6(0)

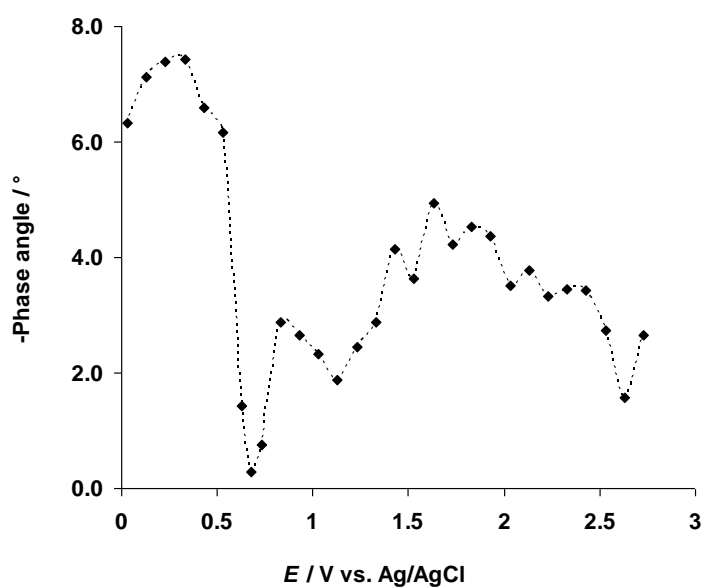
**Table S2.**  $dBE$  vs.  $dE$  (eV V<sup>-1</sup>) slopes for aliphatic carbon (C<sub>5</sub>) C 1s, initial nitrogen (N1) N 1s, initial boron (B1) B 1s, F 1s and initial bromine (Br) Br 3d<sub>5/2</sub> photoelectron binding energies measured for 5 wt% EMImBr + EMImBF<sub>4</sub> | C(Mo<sub>2</sub>C) system for various potential ranges.

	$-2.03 \text{ V} < E < -1.17 \text{ V}$	$-1.17 \text{ V} < E \leq 1.23 \text{ V}$
(C <sub>5</sub> ) C 1s	-0.50 (R <sup>2</sup> = 0.970)	-0.98 (R <sup>2</sup> = 0.995)
(N1) N 1s	-0.52 (R <sup>2</sup> = 0.924)	-0.91 (R <sup>2</sup> = 0.997)
(B1) B 1s	-0.50 (R <sup>2</sup> = 0.952)	-0.92 (R <sup>2</sup> = 0.999)
F 1s	-0.42 (R <sup>2</sup> = 0.782)	-0.87 (R <sup>2</sup> = 0.979)
(Br1) Br 3d <sub>5/2</sub>	-0.52 (R <sup>2</sup> = 0.948)	-0.72 (R <sup>2</sup> = 0.970)*

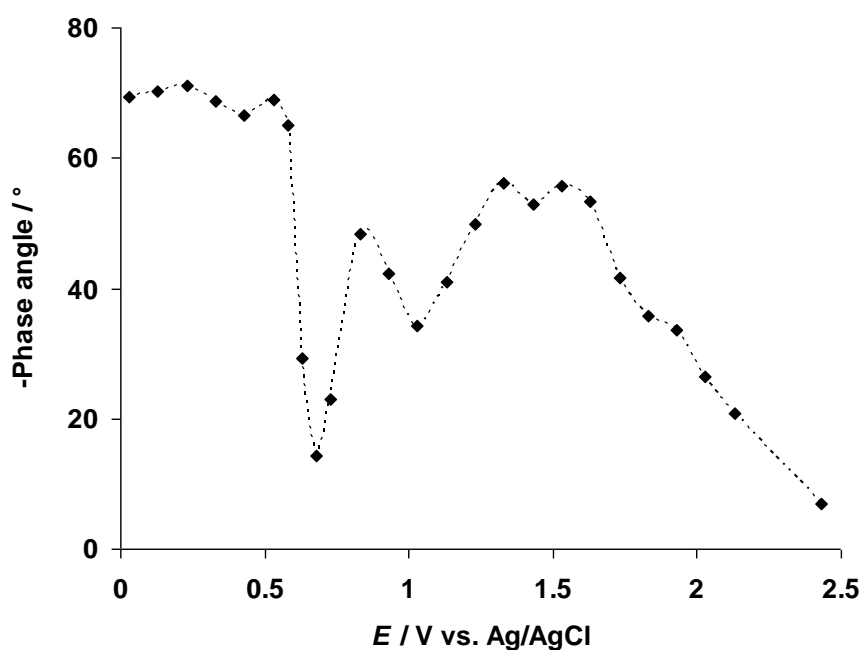
\* Calculated for the potential range  $-1.17 \text{ V} < E < 0.73 \text{ V}$ .

**Table S3.** C 1s, N 1s, B 1s, F 1s and Br 3d PE binding energies (eV) measured by *in situ* XPS for 5 wt% EMImBr + EMImBF<sub>4</sub> | C(Mo<sub>2</sub>C) system polarized at various positive potentials (corresponding spectra are shown in Figures. 10a – e).

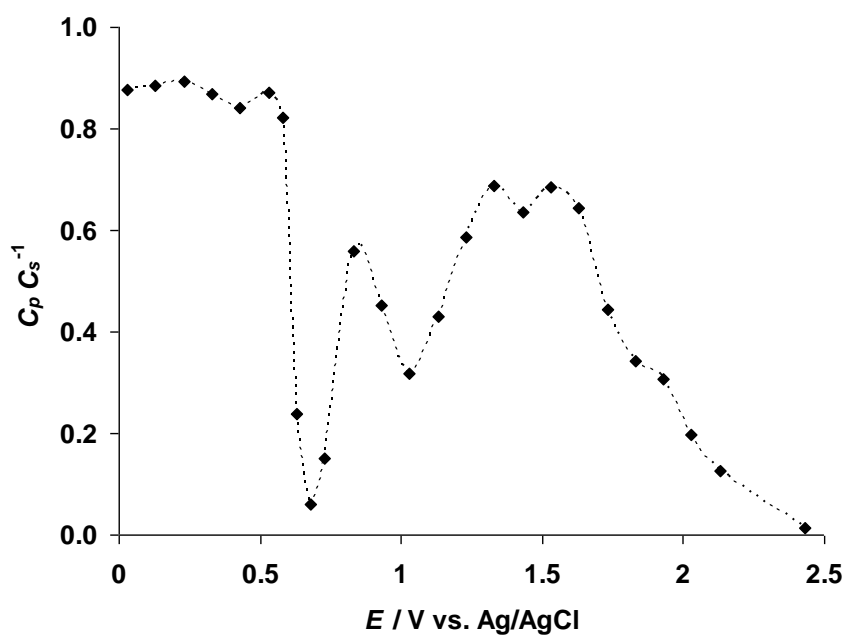
	$E = 0.03 \text{ V}$	$E = 0.73 \text{ V}$	$E = 1.03 \text{ V}$	$E = 1.23 \text{ V}$
C 1s				
C1	287.6(5)	287.1(5)	286.6(5)	286.5(5)
C2 + C3	286.9(5)	286.4(5)	285.9(5)	285.8(5)
C4 + C6	286.4(5)	285.9(5)	285.4(5)	285.3(5)
C5	285.3(5)	284.8(0)	284.1(5)	284.1(0)
N 1s				
N	402.3(0)	401.7(0)	401.1(0)	
B 1s				
B	194.0(0)	193.4(0)	192.9(0)	
F 1s				
F	687.1(0)	686.5(0)	685.8(0)	
Br 3d				
Br1 3d <sub>5/2</sub>	67.3(0)	66.7(0)	—	
Br1 3d <sub>3/2</sub>	68.3(0)	67.7(0)	—	
Br2 3d <sub>5/2</sub>	—	69.6(0)	69.0(0)	
Br2 3d <sub>3/2</sub>	—	70.4(0)	70.0(0)	



**Figure S1.** Electrochemical impedance spectroscopy phase angle data for 5 wt% EMImBr + EMImBF<sub>4</sub> solution, measured at  $\nu = 0.1 \text{ Hz}$  and at various C(Mo<sub>2</sub>C) electrode positive potentials.



**Figure S2.** Electrochemical impedance spectroscopy phase angle data for 5 wt% EMImBr + EMImBF<sub>4</sub> solution, measured at  $\nu=0.95$  mHz and at various C(Mo<sub>2</sub>C) electrode positive potentials.



**Figure S3.** The parallel capacitance ( $C_p$ ) and series capacitance ( $C_s$ ) ratio ( $C_p C_s^{-1}$ ) data at various C(Mo<sub>2</sub>C) electrode positive potentials and  $\nu=0.95$  mHz, obtained for 5 wt% EMImBr + EMImBF<sub>4</sub> | C(Mo<sub>2</sub>C) interface.



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