

Electronic Supplementary Information

Redox-active Ionic Liquid Electrolyte with Multi Energy Storage Mechanism for High Energy Density Supercapacitor

Duck-Jea You^a, Zhenxing Yin^a, Yong-keon Ahn^b, Seong-Hun Lee^a, Jeeyoung Yoo^{*a} and Youn Sang Kim^{*a,c}

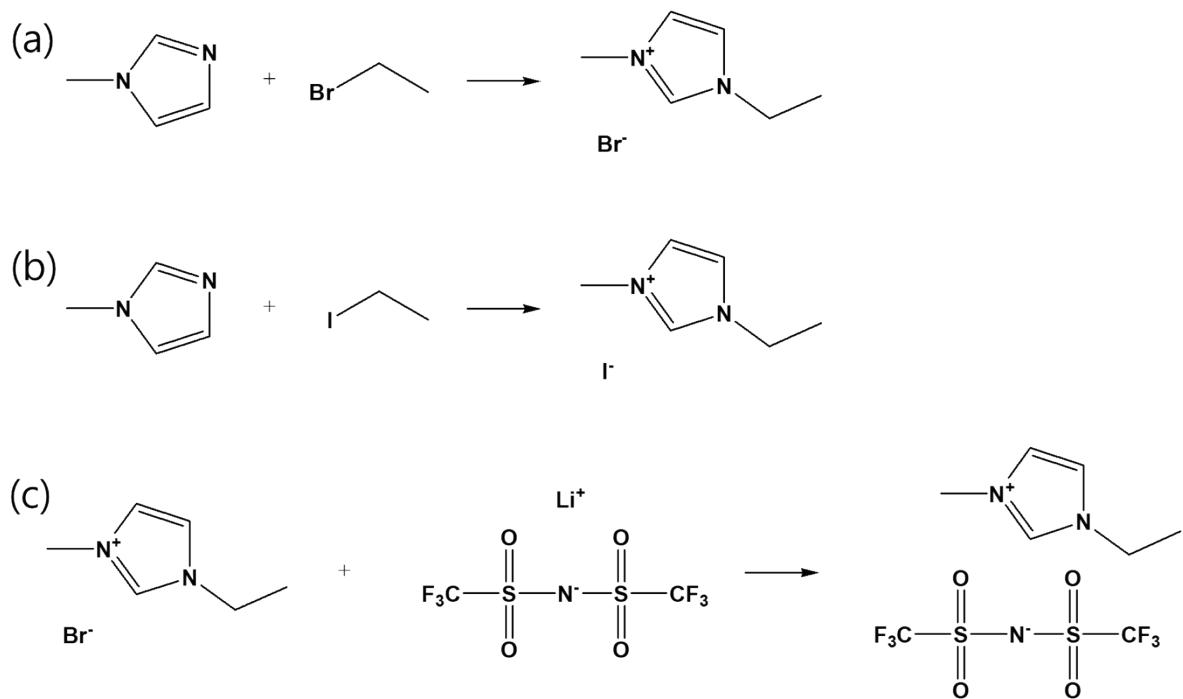


Fig.S1. Reaction mechanism of (a) EMI-Br, (b) EMI-I and (c) EMITFSI

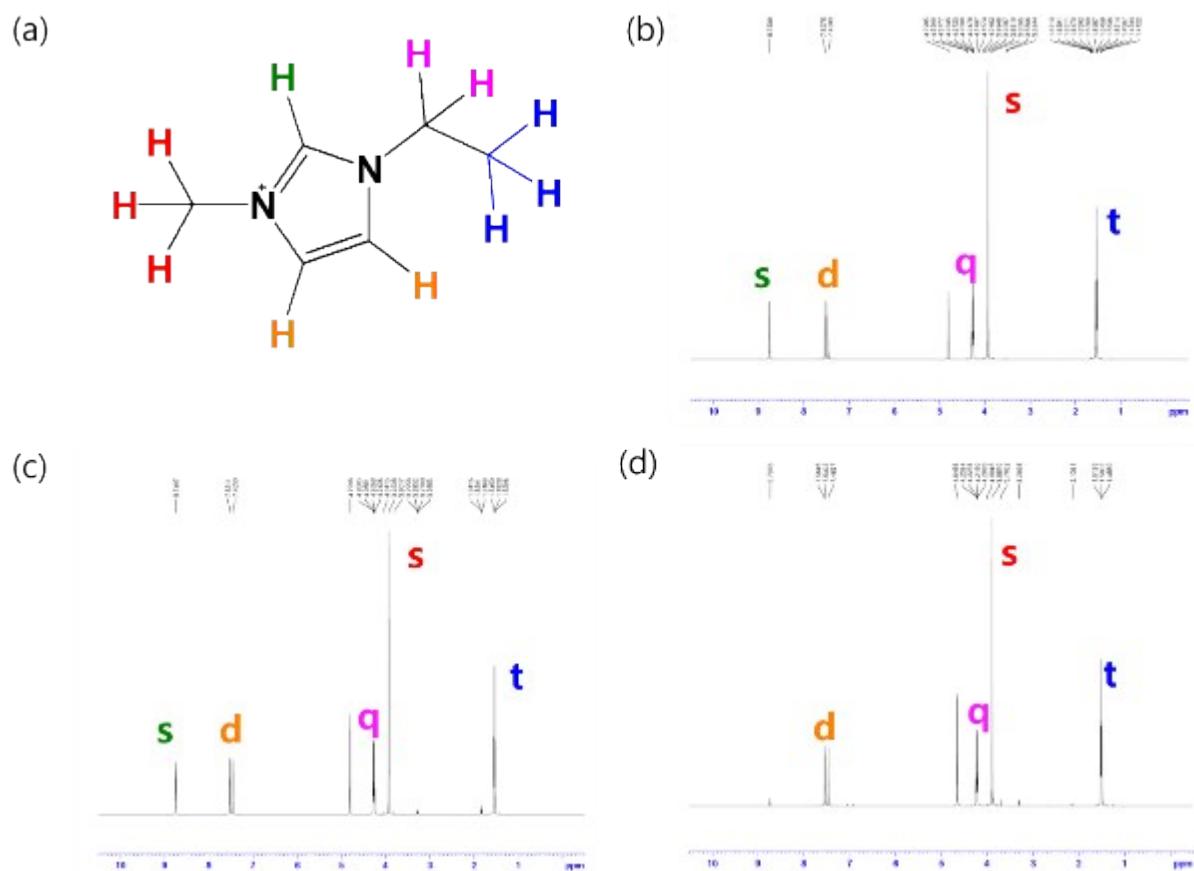
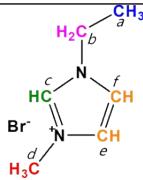
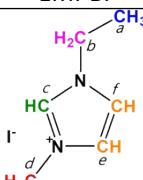
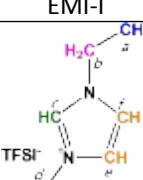


Fig. S2. (a) Cation structure, ^1H NMR of (b) EMI-Br, (c) EMI-I and (d) EMITFSI (abbreviated as follows: s=singlet, d = doublet, t = triplet and q = quartet)

Table S1. ^1H NMR Data of EMI cation

	Proton	Shift (δ) [ppm]	Multiplicity	Integration
	a	1.5987	Triplet	3.293
EMI-Br	b	4.2723	Quartet	2.210
	c	8.7539	Singlet	1.975
	d	4.0462	Singlet	3.306
	e, f	7.4597	doublet	1.975
	a	1.5328	Triplet	3.587
EMI-I	b	4.2558	Quartet	2.378
	c	8.7497	Singlet	1.000
	d	3.9238	Singlet	3.556
	e, f	7.4530	doublet	2.125
	a	1.5328	Triplet	3.125
EMI-TFSI	b	4.2150	Quartet	2.093
	c	ND	ND	ND
	d	4.0045	Singlet	1.000
	e, f	7.5402	doublet	1.000

*ND : Not Detected for weak intensity

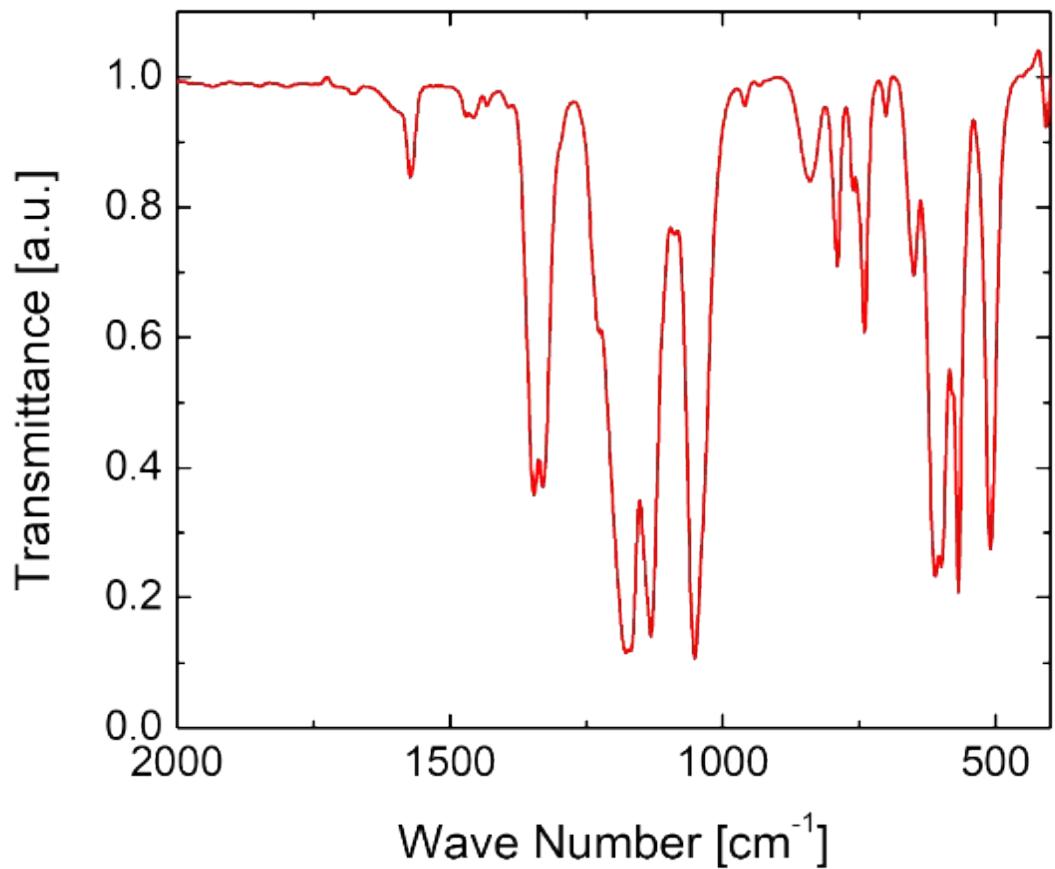


Fig. S3. ATR FTIR of TFSI anion from EMITFSI

Table S2. ATR FTIR bands location of EMITFSI

Functional groups	
N=C-N stretching vibration	1493-1437 cm ⁻¹
ring C=C vibration	1595-1546 cm ⁻¹
asymmetric vibration of CF ₃	674-581 cm ⁻¹ , 540-478 cm ⁻¹
symmetric vibration of CF ₃	579-551 cm ⁻¹

Table S3. Thermal degradation temperature of prepared electrolytes, and ionic liquids.

	1 st degradation temperature (°C)	2 nd degradation temperature (°C)
EMITFSI	445.91	-
EMI-Br	265.75	-
EMI-I	251.04	-
EMIT-Br0.04	277.79	450.8606
EMIT-Br0.08	283.7	447.8096
EMIT-Br0.12	285.01	447.384
EMIT-I0.04	267.45	442.1724
EMIT-I0.08	268.25	443.7011
EMIT-I0.12	268.56	442.0142

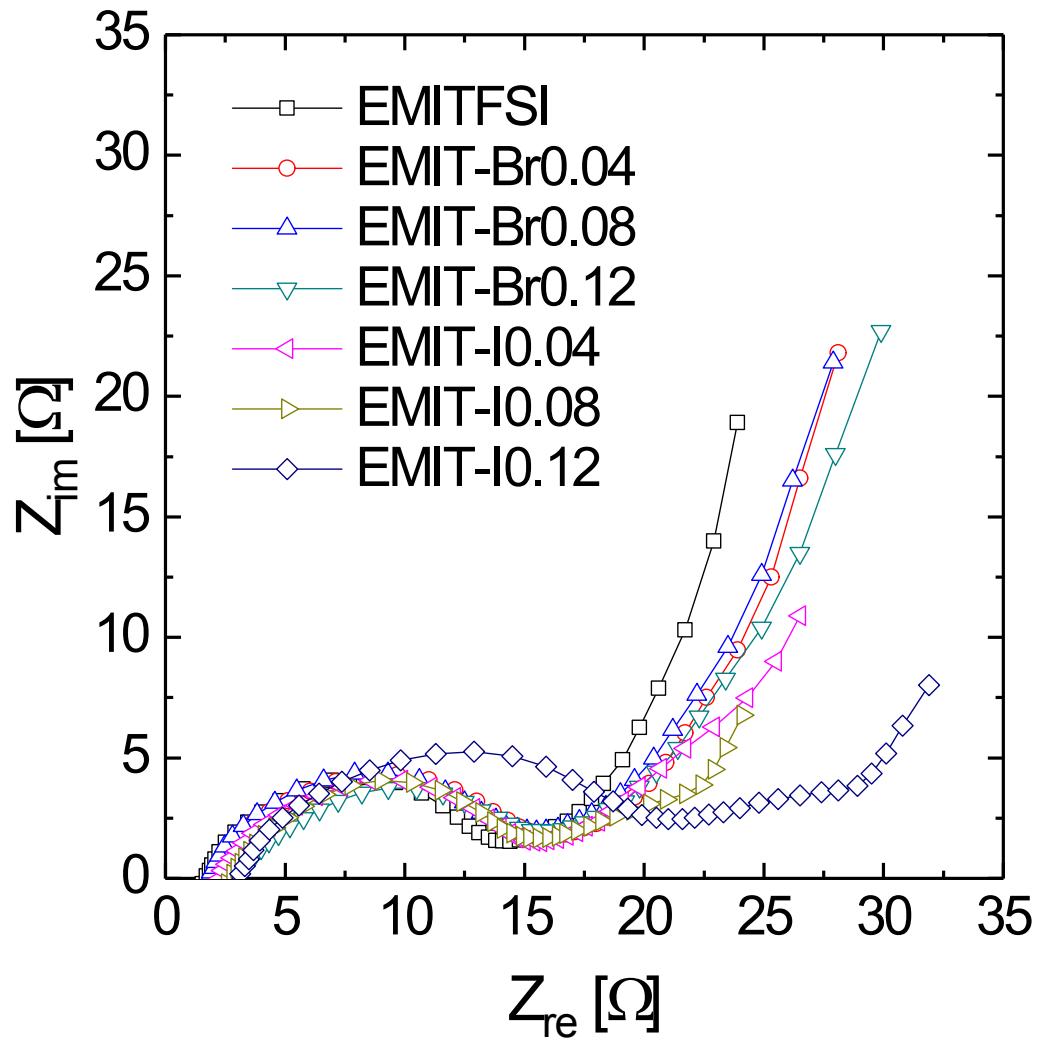


Fig. S4. Nyquist plot of EMITFSI and EMI-X added electrolyte

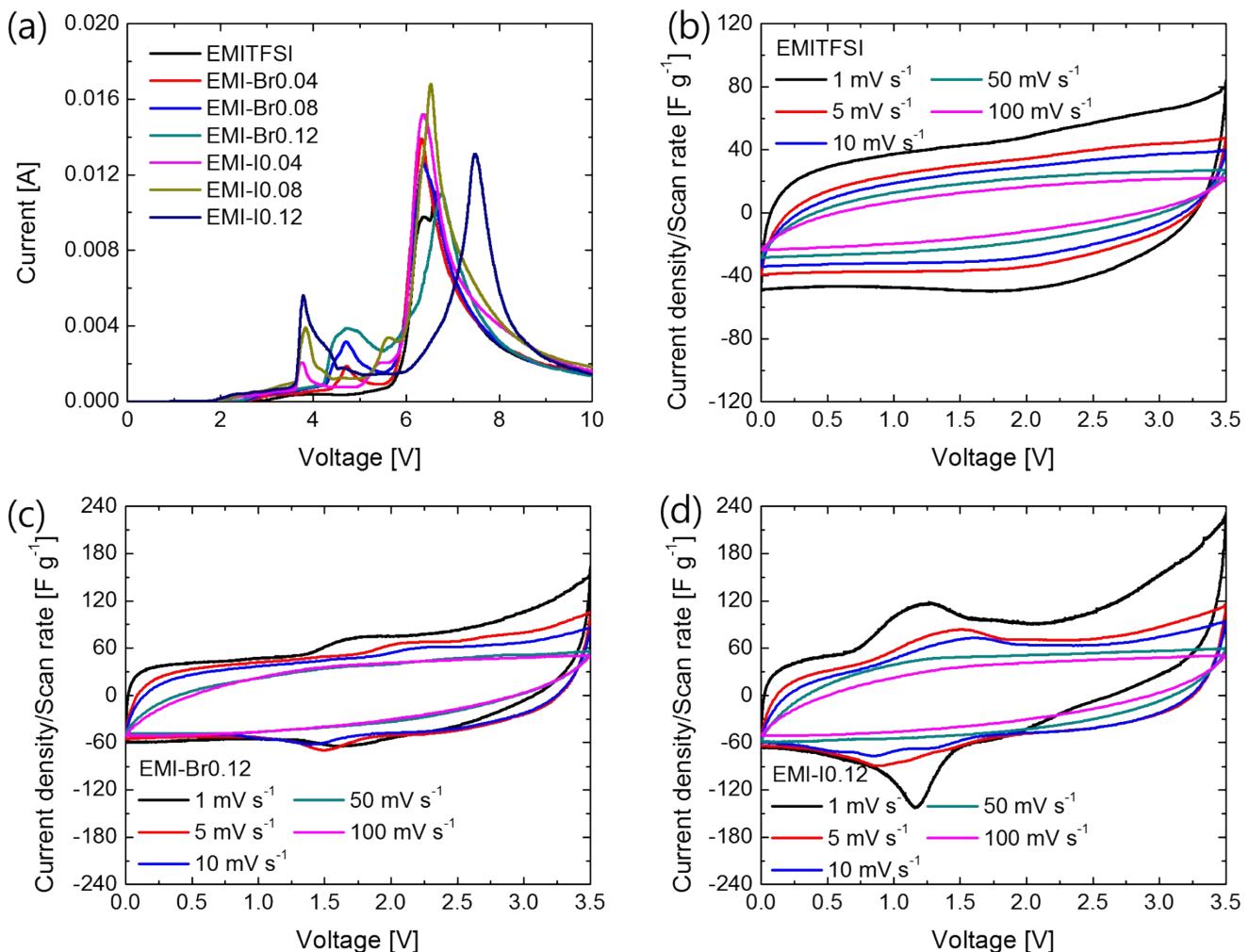


Fig. S5. (a) Linear sweep voltammograms for EMITFSI/EM-X and EMITFSI, Cyclo-voltammograms of (b) EMITFSI, (c) EMIT-Br0.12 and (d) EMIT-I0.12

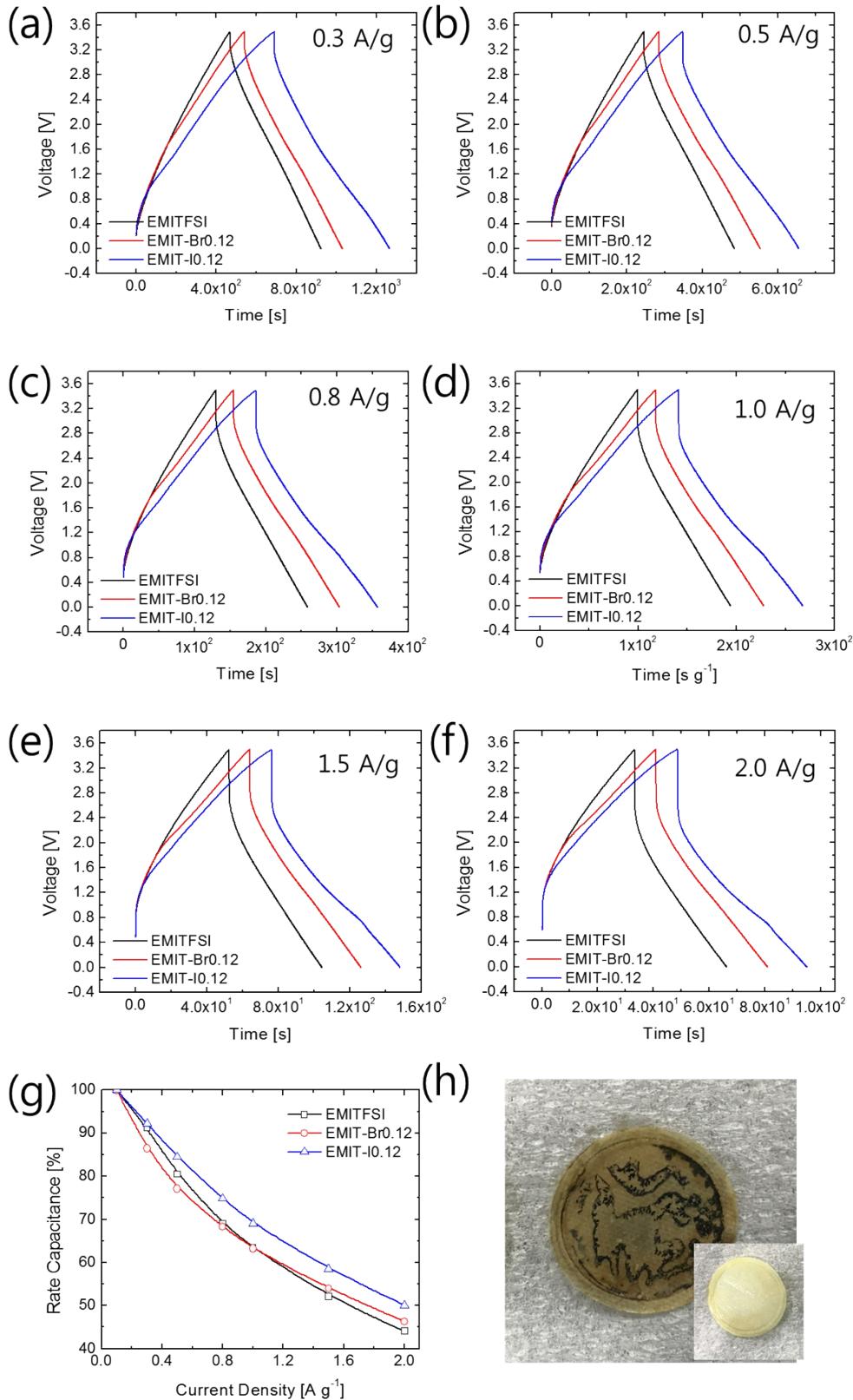


Fig. S6. The Glavanostatic charge-discharge profile of SCs adopting EMITFSI, EMIT-X with various current density (a) 0.3 A g^{-1} , (b) 0.5 A g^{-1} , (c) 0.8 A g^{-1} , (d) 1.0 A g^{-1} , (e) 1.5 A g^{-1} , (f) 2.0 A g^{-1} , (g) Capacitance fading of SCs adopting EMITFSI, EMIT-X with various current density, (h) EMIT-Br0.12 electrolyte after 300 cycle with 1 A g^{-1} (inset : EMIT-I0.12 after 5000 cycle)

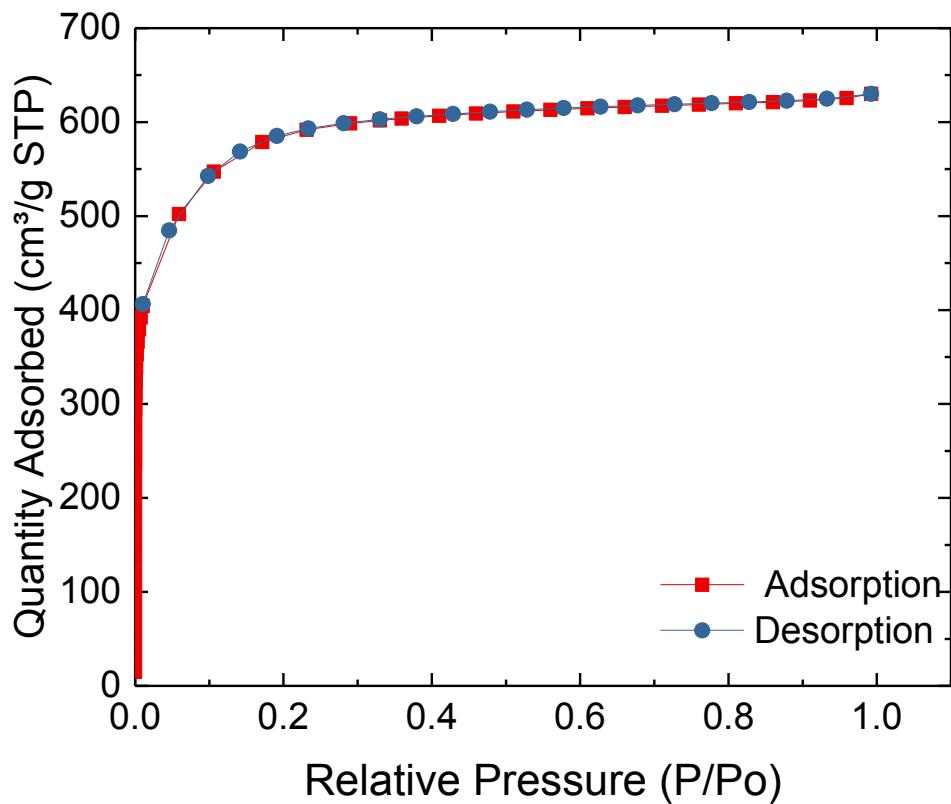


Fig. S7. N₂ (77k) adsorption-Desorption isotherm on Porous carbon

Table S4. Performance of various Ionic liquid based supercapacitor¹

Type	Material	Ionic liquid	Specific capacitance / F g ⁻¹	Rate / A g ⁻¹	Window / V	Specific energy / Wh kg ⁻¹	Specific power / kW kg ⁻¹	Cyclability / retention (Number of cycles)	Ref.
Bimodal Redox-active	Porous carbon	EMIT-I0.12 (Proposed electrolyte)	200.6	1	3.5	175.6	5	95% (15000)@1A g ⁻¹ (25C-rate)	in this study
Redox-active electrolyte	Activated carbon	EMIFcNTf/C H ₃ CN			2.5	23.7			²
Redox-active electrolyte	Activated carbon fiber cloths	EMIBr/EMIF ₄	59	0.1	1.5				³
Redox-active electrolyte	microporous-mesoporous carbon	EMIBF ₄ +EMI I	245		2.4	36.7			⁴
EDL	Porous carbon	EMIBF ₄	147	1	3	11.4	98	90% (10,000) @ 100 A g ⁻¹	⁵
EDL	Activated carbon fiber cloths	EMIBF ₄	32.6	0.1	1.5				³
EDL	Porous carbon	EMIBF ₄	147	2 mA cm ⁻²	4.0	20	3.1	97% (1,000)	⁶
EDL	SiC-derived carbon	EMIBF ₄	170	0.1	3.6				⁷
EDL	Carbon nanofibers	EMITFSI	161	1	3.5	246	30		⁸
EDL	Ti3C2Tx	EMITFSI	70	1 mV s ⁻¹	3.0				⁹
Double EDL	Carbon	EMITFSI	160	1	3.0	20	42		¹⁰
EDL	Porous carbon nanofiber	EMITFSI	180	0.5	3.5	80	0.4		¹¹
EDL	Graphene-based carbon	EMITFSI/AN	174	2	3.5	74	338	94% (1,000)	¹²
EDL	Si nanowires	BMITFSI	0.7		1.6	0.23	0.65		¹³
EDL	Carbonized cellulose/Activated carbon	BMPYTFSI	84	0.1	3.0	21	41.6	92% (10,000)	¹⁴

EDL	N-doped reduced graphene oxide aerogel	BMPDCA	765	1	4	245	6.53	86% (3,000)	¹⁵
EDL	Graphene nanosheets	BMPDCA	330		3.3	140 at 60 °C	52.5 at 60 °C		¹⁶
Pseudo	C/RuO ₂	EMIBF ₄	52	3	3.8	108		98.5% (100,000)	¹⁷
Pseudo	K10 clay	Et ₄ NBF ₄ /AN	36	2	2.7	171	1.98	90% (5,000)	¹⁸
Pseudo	ZnFe ₂ O ₄	BMISCN (aqueous)	781		1.2	156	7.11	95% (3,000)	¹⁹

EMIFcNTf: 1-ethyl-3-methylimidazolium ferrocenylsulfonyl-(trifluoromethylsulfonyl)-imide,

EMIBF₄: 1-Ethyl-3-methylimidazolium tetrafluoroborate

EMITFSI: 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide

BMPYTFSI: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

BMPDCA: 1-butyl-1-methylpyrrolidinium dicyanamide

AN: acetonitrile

K10: acid-leached montmorillonite

Et₄NBF₄: tetraethylammonium tetrafluoroborate

MB: 1-methyl-3-butylimidazolium bromide

BMISCN: 1-butyl-3-methylimidazolium thiocyanate

BMIBF₄: 1-butyl-3-methylimidazolium tetrafluoroborate

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