SUPPORTING INFORMATION

Exploring the Versatility of Membrane-Free Battery Concept Using Different Combinations of Immiscible Redox Electrolytes

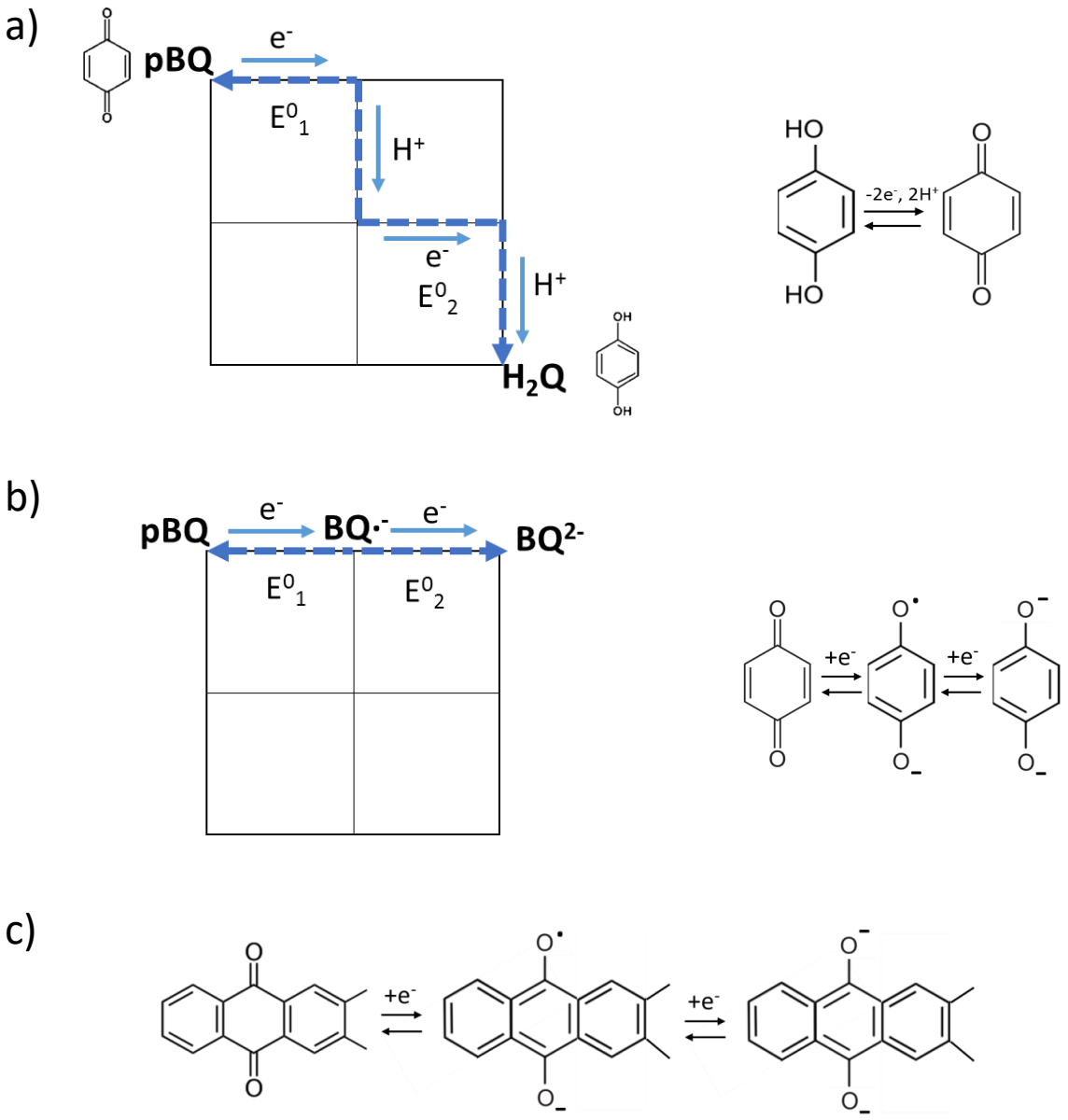
*Paula Navalpotro[†], Noemí Sierra[†,‡], Carlos Trujillo[†,¥], Iciar Montes[†], Jesus Palma[†] and Rebeca Marcilla[†]**

[†] Electrochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, 28935 Móstoles, Spain

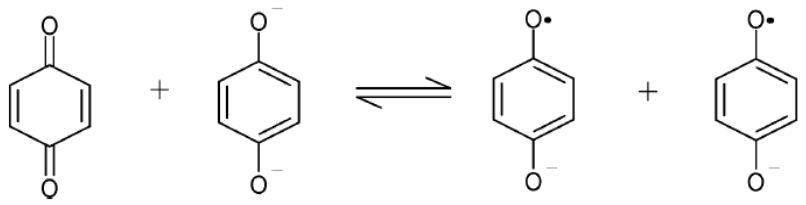
[‡] Chemical and Environmental Engineering Group, Rey Juan Carlos University C/Tulipán s/n, 28933 Móstoles, Madrid, Spain

[¥] Faculty of Chemical Science and Technology, University of Castilla-La Mancha, Avda. Camilo José Cela 10, 13071 Ciudad Real, Spain

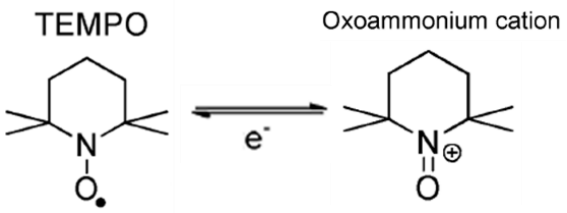
*Corresponding Author. E-mail: rebeca.marcilla@imdea.org; telephone:+0034917371131



Scheme S1. a) Scheme-of-squares and redox reaction for pBQ- H_2Q in acidic electrolyte. Horizontal movement indicates electron transfer and vertical indicates proton transfer. b) Scheme-of-squares and redox reaction of quinones in aprotic electrolytes. c) Reaction mechanism for 2,3-DMAQ in aprotic electrolytes.



Scheme S2. Comproportionation process mechanism for pBQ.



Scheme S3. Redox reaction mechanism for TEMPO in 0.1M NaCl

Table S1. Diffusion Coefficients and kinetic rate constants of the different electrolytes.

	Electrolyte	Battery	D (cm^2s^{-1})	K^0 (cms^{-1})
Anolytes	pBQ in $PYR_{14}TFSI$ [35]	Proof-of-concept Battery E	$5.8\cdot10^{-5}$	$1.2\cdot10^{-3}$
	2,3DMAQ in $PYR_{14}TFSI$	Battery A, G	$1.49\cdot10^{-7}$	$2.98\cdot10^{-4}$
	OilBlueN in $PYR_{14}TFSI$	Battery B, H	$5.10\cdot10^{-8}$	$1.09\cdot10^{-4}$
	pBQ in 0.1 M $TBAPF_6$ – PC	Battery D, J	$2.12\cdot10^{-6}$	$3.21\cdot10^{-3}$
	pBQ in PC+$PYR_{14}TFSI$	Battery F	$3.9\cdot10^{-6}$	$1.5\cdot10^{-3}$
Catholytes	H_2Q in 0.1M HCl [35]	Proof-of-concept Battery A, B, C and D	$4.1\cdot10^{-4}$	0.379
	TEMPO in 0.1M NaCl	Battery E	$6.6\cdot10^{-6}$	$3.82\cdot10^{-4}$
	OH-TEMPO in 0.5M NaCl	Battery F-J	$7.12\cdot10^{-6}$	$5.23\cdot10^{-4}$

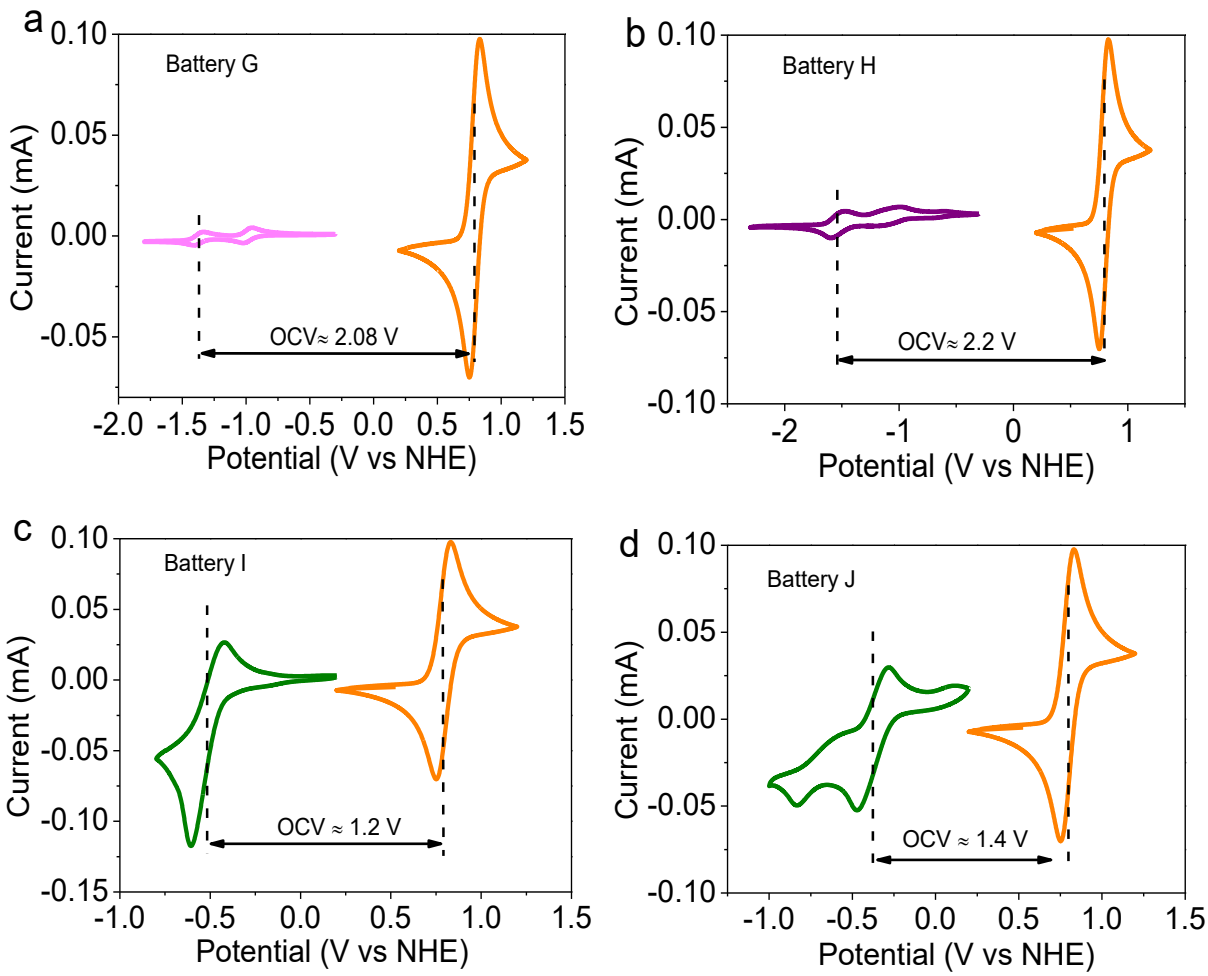
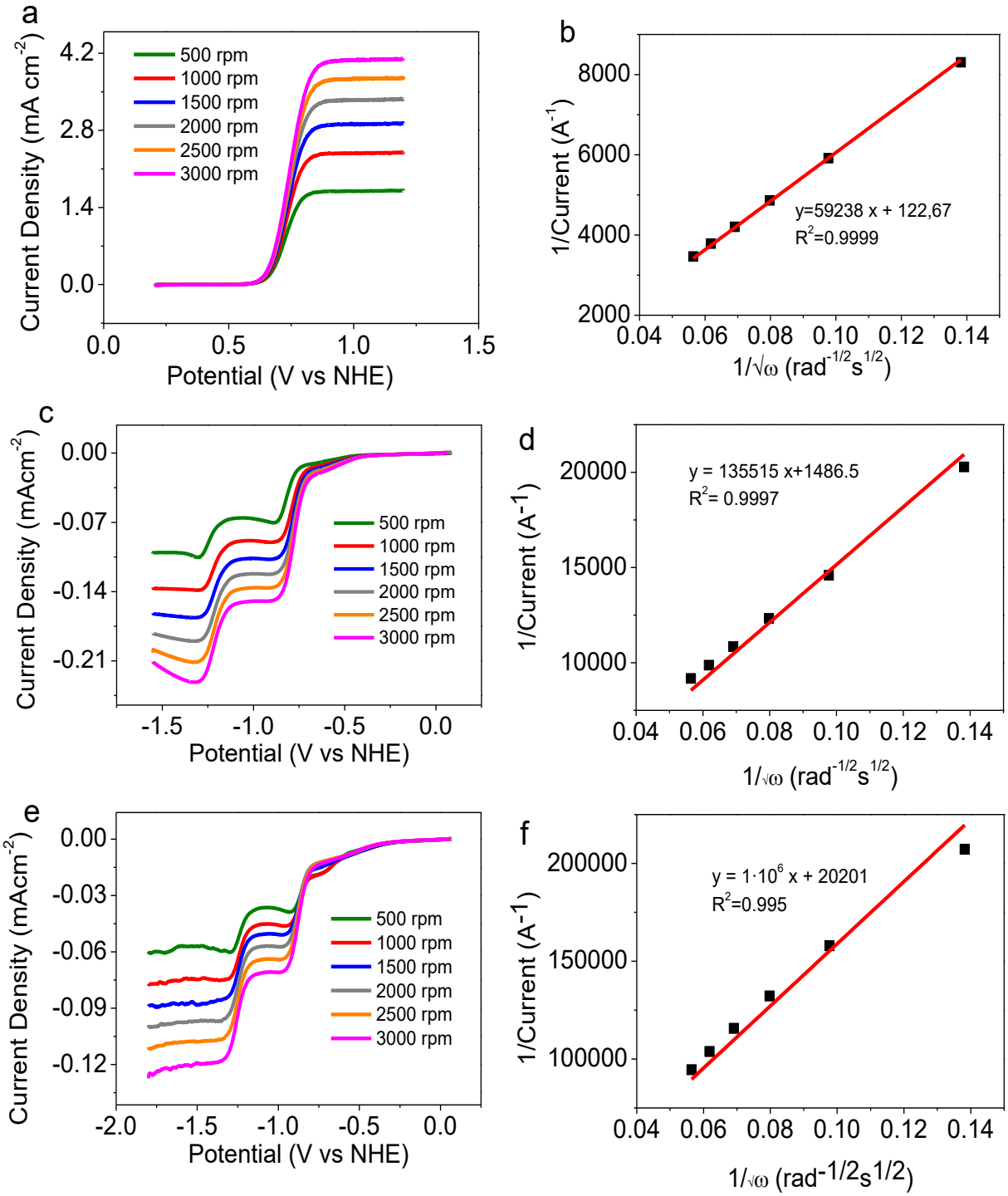


Figure S1. CVs of pairs of immiscible anolyte and catholyte for a) Battery G, b) Battery H, c) Battery I, and d) Battery J. (pBQ in green, OH-TEMPO in orange, 2,3DMAQ in pink, OilBlue N in purple). The composition of electrolytes is 20 mM of redox active specie. Scan rate: 10 mVs^{-1}


a
Current Density (mA cm-2)
Potential (V vs NHE)
500 rpm
1000 rpm
1500 rpm
2000 rpm
2500 rpm
3000 rpm
b
1/Current (A-1)
1/√ω (rad-1/2s1/2)
y=59238 x + 122,67
R2=0.9999
c
Current Density (mAcm-2)
Potential (V vs NHE)
d
1/Current (A-1)
1/√ω (rad-1/2s1/2)
y = 135515 x+1486.5
R2= 0.9997
e
Current Density (mAcm-2)
Potential (V vs NHE)
f
1/Current (A-1)
1/√ω (rad-1/2s1/2)
y = 1·106 x + 20201
R2=0.995

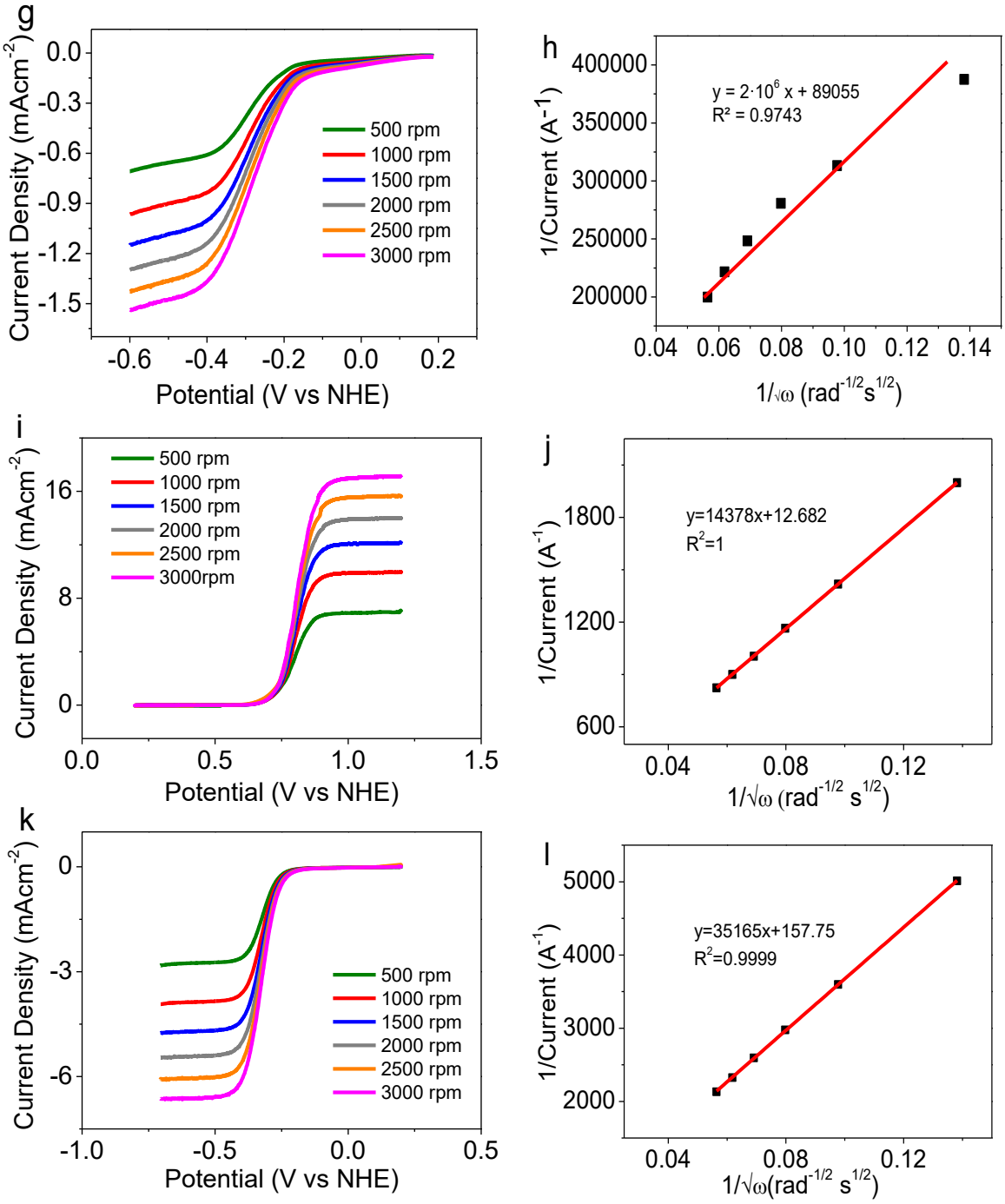


Figure S2. Rotating Disk Electrode experiments. a), b) LSV at 10 mVs^{-1} and Levich plot (the mass-transport limited current vs. the square root of the rotation rate) of 5 mM TEMPO in 0.1M NaCl. c), d) LSV at 10 mVs^{-1} and Levich plot of 5 mM 2,3DMAQ in $PYR_{14}TFSI$. e), f) LSV at 10 mVs^{-1} and Levich plot of 5mM OilBlue N in $PYR_{14}TFSI$. g), h) LSV at 10 mVs^{-1} and Levich plot of 5 mM pBQ in PC (0.1 M $TBAPF_6$). i), j) LSV at 10 mVs^{-1} and Levich plot of 5mM OH-TEMPO (0.5 M NaCl). k), l) LSV at 10 mVs^{-1} and Levich plot of 5 mM pBQ in PC:$PYR_{14}TFSI$ (75:25 %w).

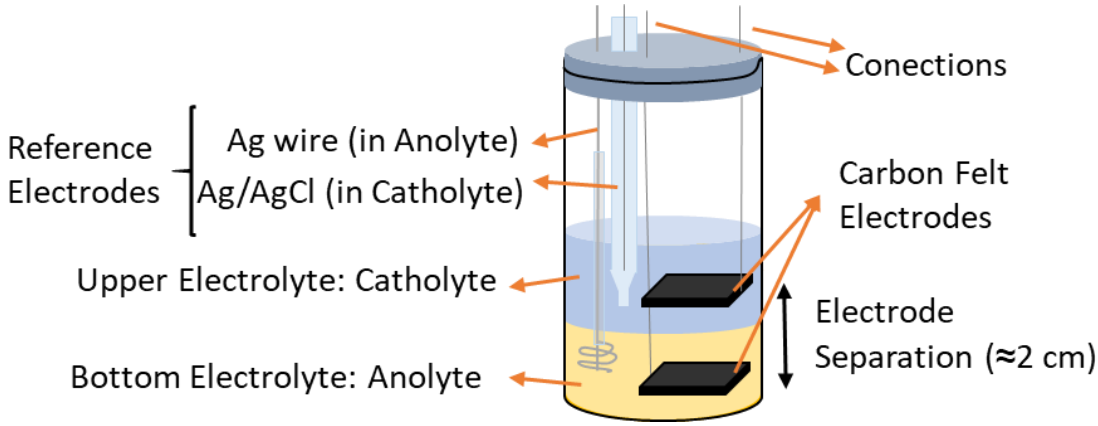


Figure S3. Schematic illustration of the battery assembly

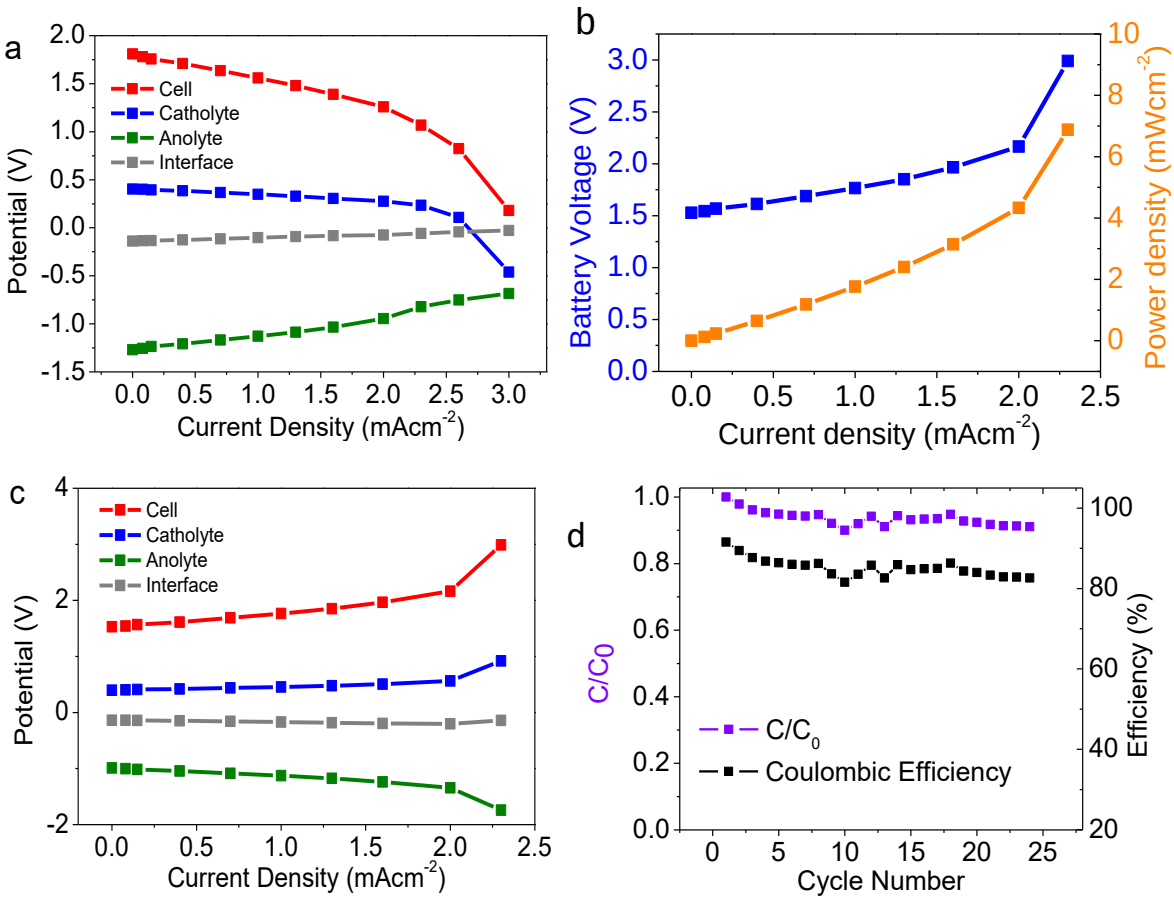


Figure S4. Electrochemical characterization Battery A (35% SOC). Active species concentration: 20 mM in catholyte and anolyte. a) Discharge polarization test of battery and each individual profile (catholyte, anolyte and interface) b) Polarization test during charge. c) Individual voltages profiles of the cell, individual electrolytes and the interface during polarization test in charge. d) Cycling stability over 25 cycles.

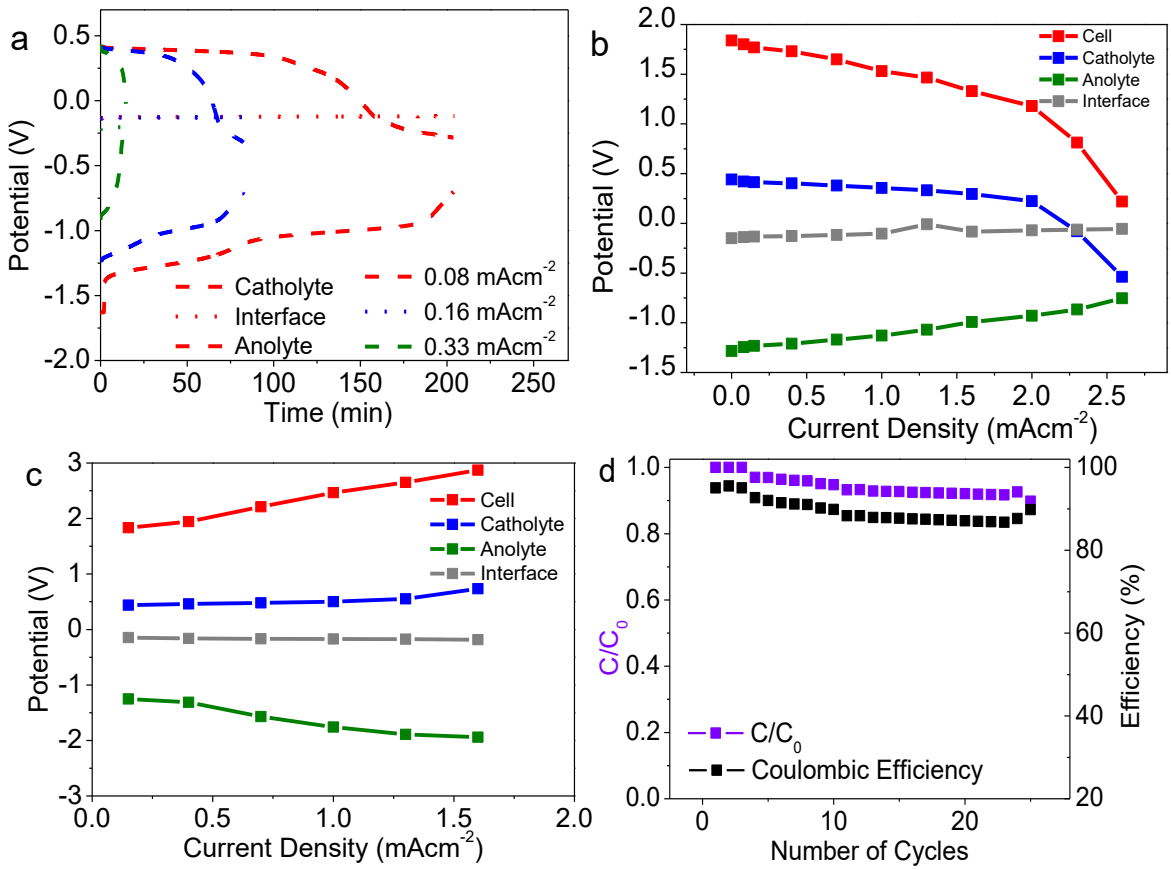


Figure S5. Performance of the Battery B (SOC 35 %). Active species concentration: 20 mM in catholyte and anolyte. a) Discharge curves of the individual potential profiles of each electrolyte and interface at different current densities. b) Discharge polarization test of battery and each individual profile (catholyte, anolyte and interface). c) Individual voltages profiles of the cell, individual electrolytes and the interface during polarization test in charge. d) Cycling stability over 25 cycles.

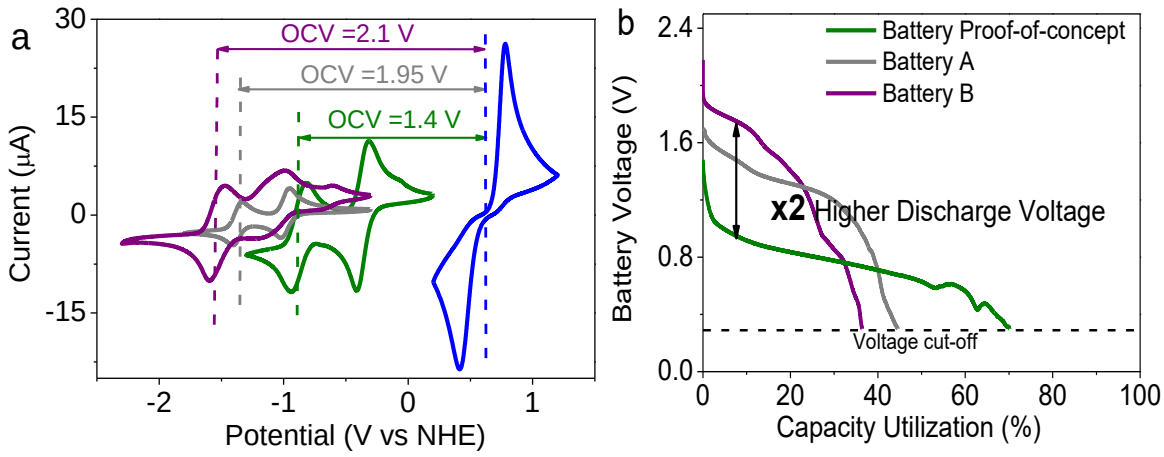


Figure S6. a) Comparison of CV for the anolytes and the catholye used in the Batteries A, B and Proof-of-concept (H_2Q in 0.1 M HCl in blue, 2,3-DMAQ in $PYR_{14}TFSI$ in grey, OilBlue N in $PYR_{14}TFSI$ in purple and pBQ in $PYR_{14}TFSI$ in green). b) Comparison between potential-capacity discharge profile at 0.08 $mAcm^{-2}$ (35%SOC) for Batteries A,B and Proof-of-concept.

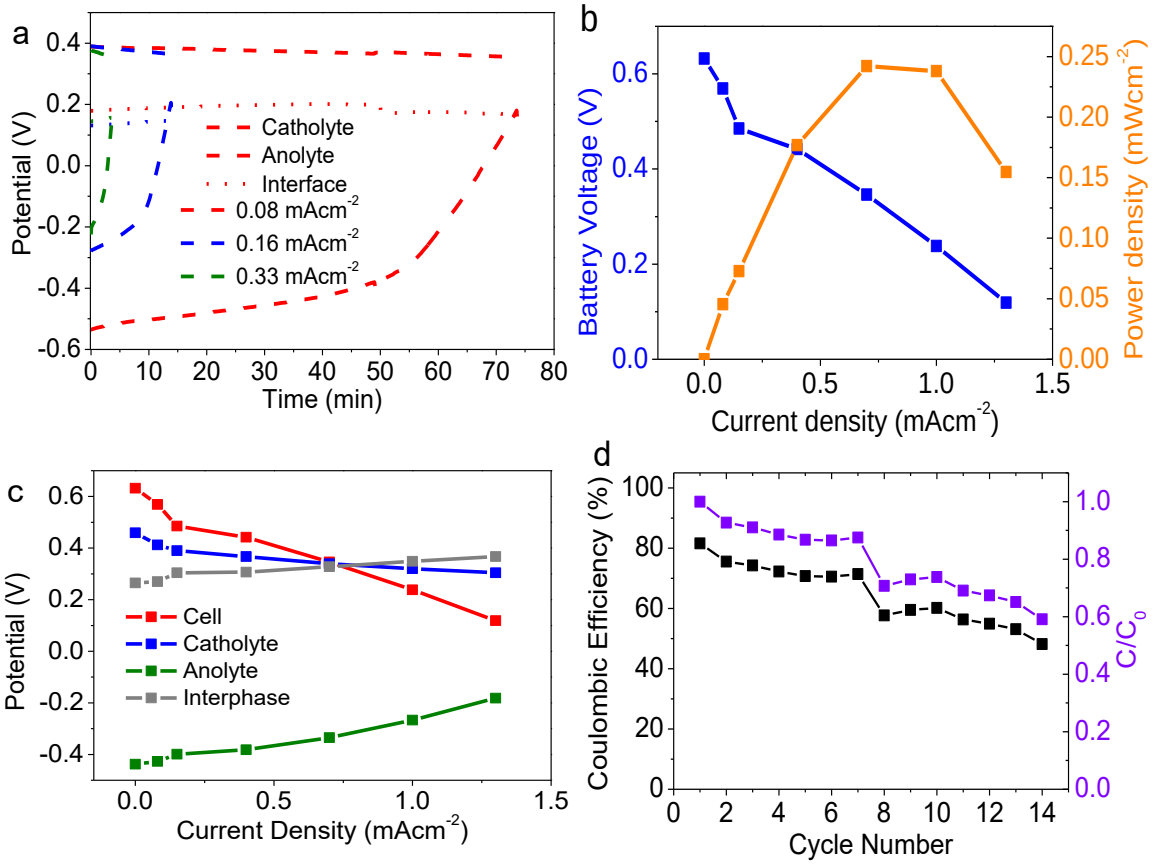


Figure S7. Electrochemical behavior of Battery D (SOC 25%). Active species concentration: 20 mM in catholyte and anolyte. a) Discharge individual voltage profiles of each electrolyte and the interface at different current densities. b) Polarization test during discharge. c) Discharge polarization test of battery and each individual profile (catholyte, anolyte and interface). d) Cycling stability (5 %SOC) at 0.16 $mAcm^{-2}$

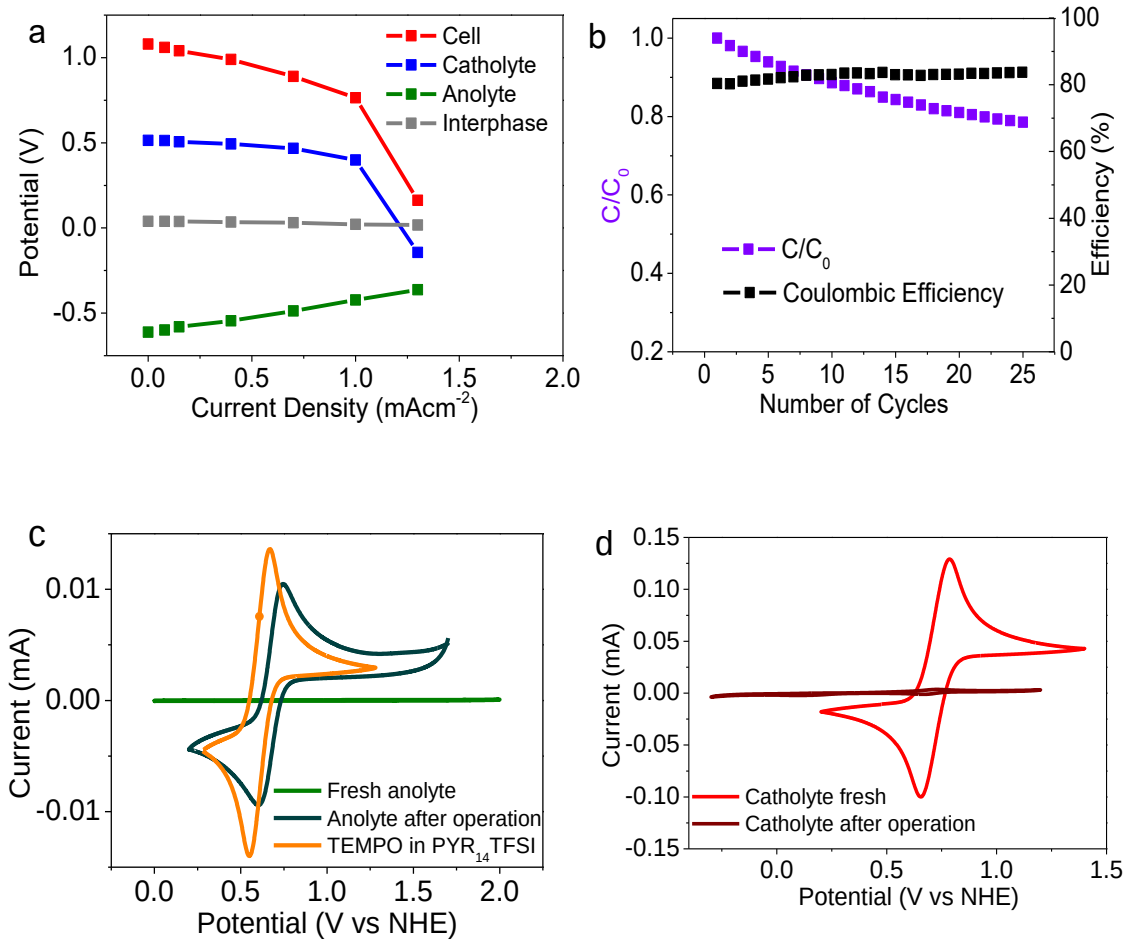


Figure S8. Performance of the Battery E. Active species concentration: 40 mM in catholyte and 20 mM in anolyte. a) Discharge polarization test of battery and each individual phase (catholyte, anolyte and interface) at 35% SOC. b) Cycling stability (5 %SOC) at 1 $mAcm^{-2}$ for charging and 2 $mAcm^{-2}$ for discharging. c) CV of the anolyte at positive potential range before operating (light green) and after battery operation (dark green), for comparison CV of TEMPO in $PYR_{14}TFSI$ at 20 mM concentration was also included (orange).d) CV of the catholyte before (red) and after operation (dark red).

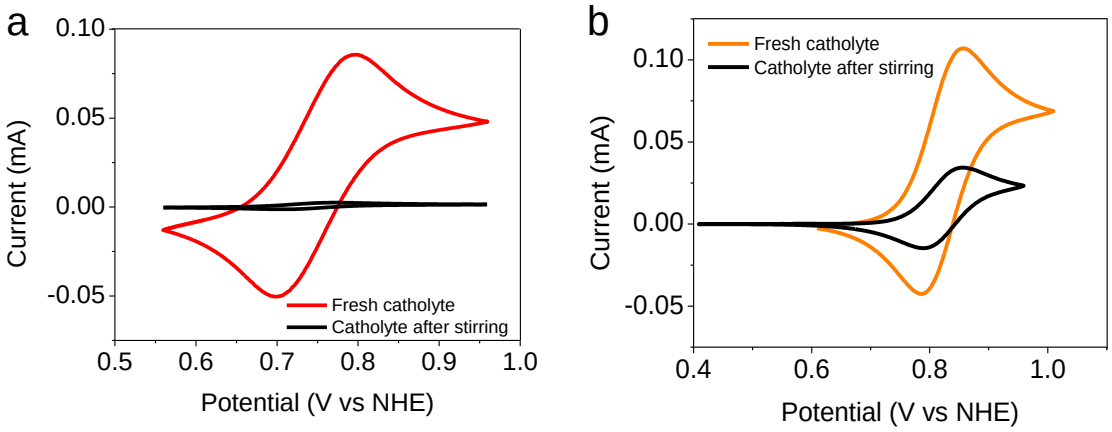


Figure S9. a) Comparison of CV of as-prepared catholyte and CV of catholyte after battery assembly for battery E (20 mM TEMPO in 0.1M NaCl), b) Comparison of CV of as-prepared catholyte and CV of catholyte after battery assembly for battery F (20 mM OH-TEMPO in 0.5M NaCl).

Table S2. Summary of Battery Performance Results

Battery	Anolyte (-)	Catholyte (+)	[Active Species]	OCV (V)	Power Density ($mWcm^{-2}$)	Operating Voltage (V)	Main changes/ Main innovation
Previous Work [35]	pBQ in $PYR_{14}TFSI$	H_2Q in 0.1 M HCl (aq)	20mM / 0.1M	1.4	1.85	0.9	Proof- of concept
A	2,3DMAQ in $PYR_{14}TFSI$	H_2Q in 0.1 M HCl (aq)	20mM	1.95	3	1.35	Different redox organic molecule in the anolyte/ Higher battery voltage and power density
B	Oilblue N in $PYR_{14}TFSI$	H_2Q in 0.1 M HCl (aq)	20mM	2.1	2.5	1.75	
D	pBQ in PC (0.1 M $TBAPF_6$)	H_2Q in 0.1 M HCl (aq)	20mM	1.0	0.25	0.55	Common and cheaper solvent in the anolyte/ Less-expensive battery
E	pBQ in $PYR_{14}TFSI$	TEMPO in 0.1 M NaCl (aq)	20mM	1.5	0.8	1.4	Different redox organic molecule and neutral media/ Higher battery voltage and less-corrosive catholyte
F	pBQ in PC +$PYR_{14}TFSI$ (75+25 %w)	OH-TEMPO in 0.5 M NaCl(aq)	0.1M	1.0	0.9	0.6	Cheaper anolyte and more soluble redox compound in the neutral catholyte/, less-corrosive and more concentrated catholyte, less-expensive battery