Supporting Information

Effect of urea as electrolyte additive for stabilization of lithium metal electrodes

*Hee-Sang Kim, Rakesh Verma, Jaekook Kim, and Chan-Jin Park **

Department of Materials Science and Engineering, Chonnam National University, 77,

Yongbongro, Bukgu, Gwangju 61186, South Korea

*** Corresponding author.**

Tel.: +82-62-530-1704. Fax: +82-62-530-1699.

E-mail address: parkcj@jnu.ac.kr (C.J. Park)

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Table S1. Fitted parameters based on equivalent circuit models (**Fig.S2**) that correspond to impedance of Li symmetric cell with 0.5 M urea additive.

Sample	R_s	R_{SEI}	CPE_{SEI}		R_{ct}	CPE_{dl}	
	(Ω)	(Ω)	C_{SEI}(F)	n_{SEI}	(Ω)	C_{dl} (F)	n_{dl}
After 1st cycle	7.52	1127.2	9.94×10^{-4}	0.638	858.7	1.03×10^{-5}	0.790
After 5th cycles	8.28	22.58	6.96×10^{-5}	0.770	51.0	4.39×10^{-6}	0.889
After 10th cycles	8.28	22.56	6.97×10^{-5}	0.770	51.1	4.38×10^{-6}	0.890
After 50th cycles	8.87	16.18	2.56×10^{-5}	0.797	6.00	7.26×10^{-6}	1.021

Table S2. Fitted parameters based on equivalent circuit models (**Fig. S2**) that correspond to impedance of Li symmetric cell without 0.5 M urea additive.

Sample	R_s	R_{SEI}	CPE_{SEI}		R_{ct}	CPE_{dl}	
	(Ω)	(Ω)	C_{SEI}(F)	n_{SEI}	(Ω)	C_{dl} (F)	n_{dl}
After 1st cycle	10.08	19.66	3.37×10^{-2}	0.448	19.86	2.18×10^{-5}	0.829
After 5th cycles	6.46	22.48	1.99×10^{-4}	0.545	9.60	5.92×10^{-2}	0.736
After 10th cycles	64.62	867.0	8.59×10^{-6}	0.445	834.11	2.96×10^{-2}	0.157

Table S3. Binding energies of C 1s, O 1s F 1s, S2p3/2, and N 1s analogous to the fitted peaks of the Li electrode from the Li symmetric cell.

Components	Binding energy (eV)				
	C1s	O1s	F1s	S2p3/2	N1s
Hydrocarbon	285				
LiTFSI	292.6		688.5	168.7	399.4
Li_2O		528.8			
LiF			684.9		
Li_3N					397
Li_2S				161.2	
$Li_2S_2O_4$				166.2	
Li_2SO_4				169.7	
Polysulfur				163.8	
Li_2CO_3	290.3	531.8			
-COO	287-288	532.3			
C=O	286.1-287.1	533.6			
$(NH_2)_2CO$	288.7	535.0			399.5

Table S4. Vibrational frequencies and assignments for bis(trifluoromethane sulfonyl)imide lithium salt (LiTFSI) and urea.

LiTFSI		Urea	
Wavenumber (cm^{-1})	Vibrational mode	Wavenumber (cm^{-1})	Vibrational mode
2876	ϑ S-CF_3	3430	ϑ N-H
1325	ϑ C-SO_2-N	3332	ϑ_{as} NH_2
1244	ϑ_{as} SO_2	3256	ϑ_{s} NH_2
1198	ϑ_{as} CF	1675	δ_{s} NH_2
1141	ϑ C-SO_2-N	1619	δ_{as} NH_2
1061	ϑ_{as} S-N-S	1590	ϑ_{s} C=O
811	δ_{s} CF_3	1458	ϑ C-N
747	ϑ S-N		
635	δ_{s} O-S-O		
572	δ_{as} CF_3		
512	δ_{as} O-S-O		

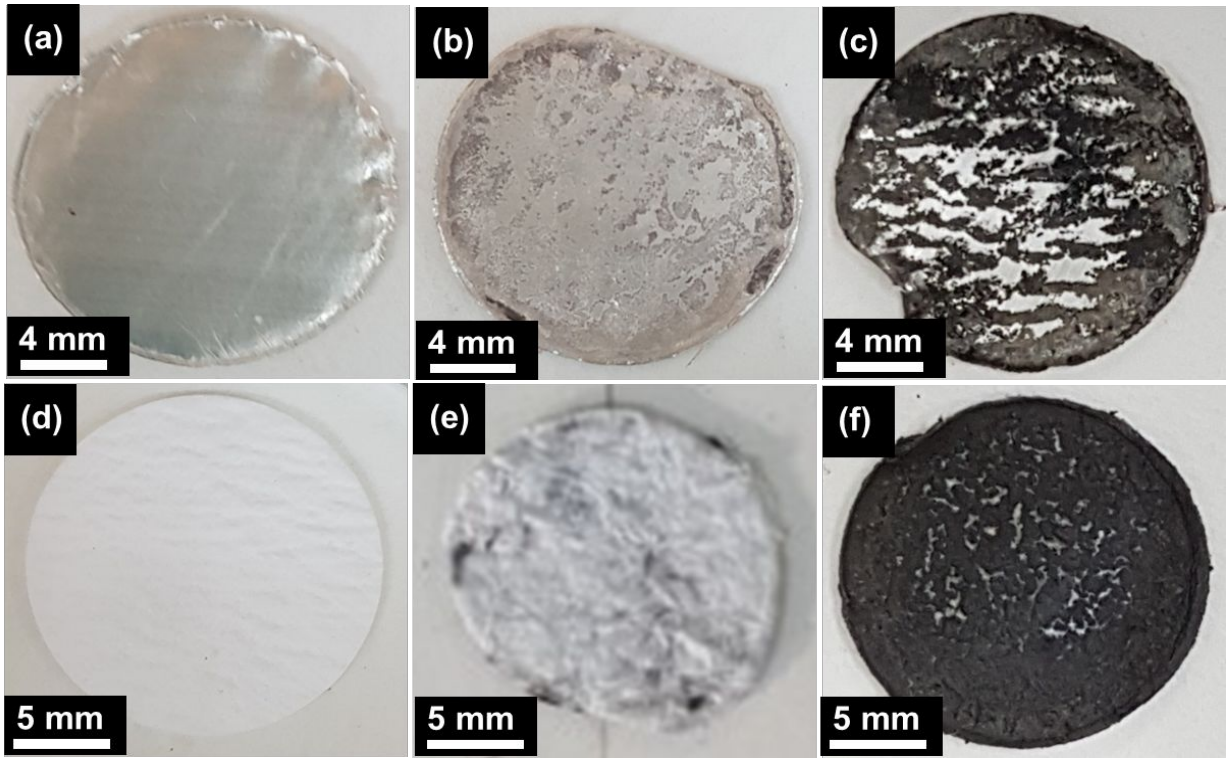

Figure S1. Typical images of components of Li symmetric cells: (a) pristine Li metal; Li metals from cells (b) with and (c) without 0.5 M urea additive; (d) pristine separator; (e) separator from cells (e) with and (f) without 0.5 M urea additive. The cells were cyclic tested for 10 cycles at current density of 1.0 mA cm^{-2}; each discharge-charge cycle lasted 2 h.

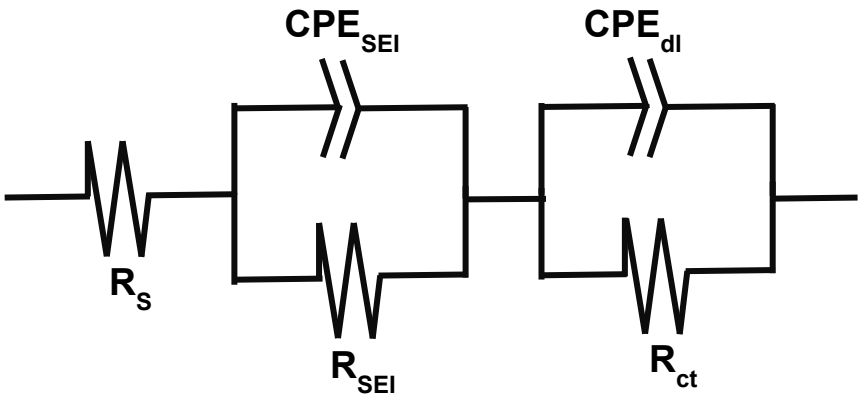

Figure S2. Equivalent circuit for electrochemical impedance spectroscopy curve of Li/Li symmetric cell. Here, R_s, R_{SEI}, and R_{ct} denote the electrolyte resistance, solid electrolyte interphase (SEI) layer resistance attributed to reaction products found on the surface of Li electrode, and charge transfer resistance, respectively; and CPE_{SEI} and CPE_{dl} denote the corresponding constant phase elements.

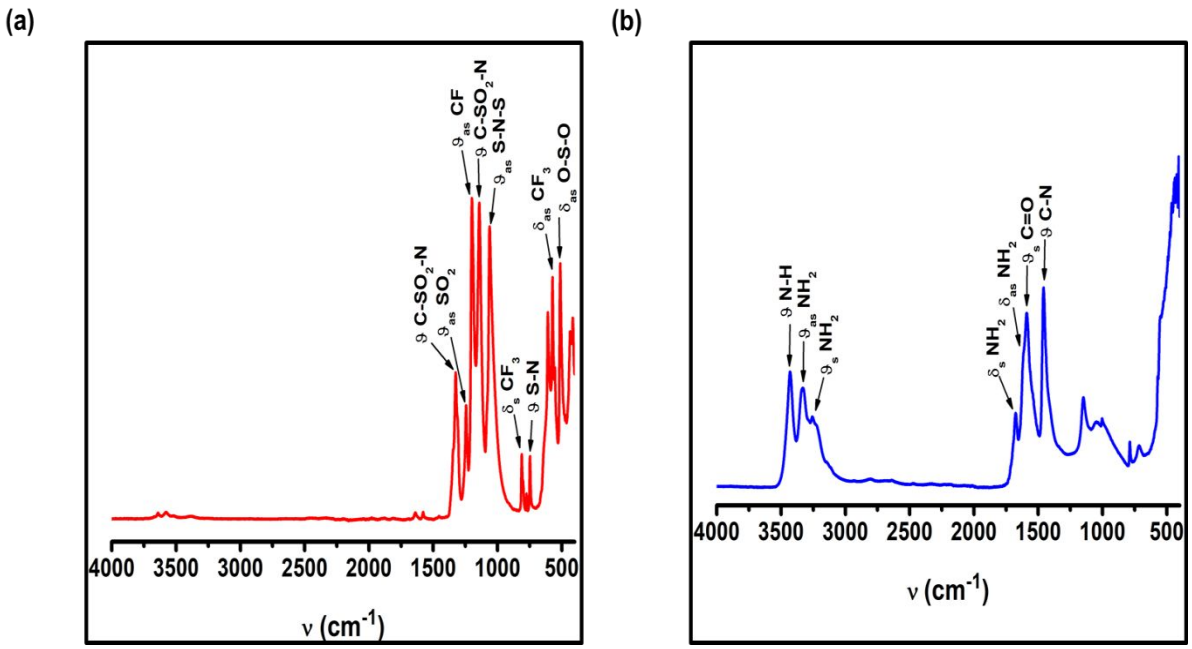

Figure S3. Fourier-transform infrared spectra of (a) pure bis(trifluoromethane sulfonyl)imide lithium salt and (b) urea.

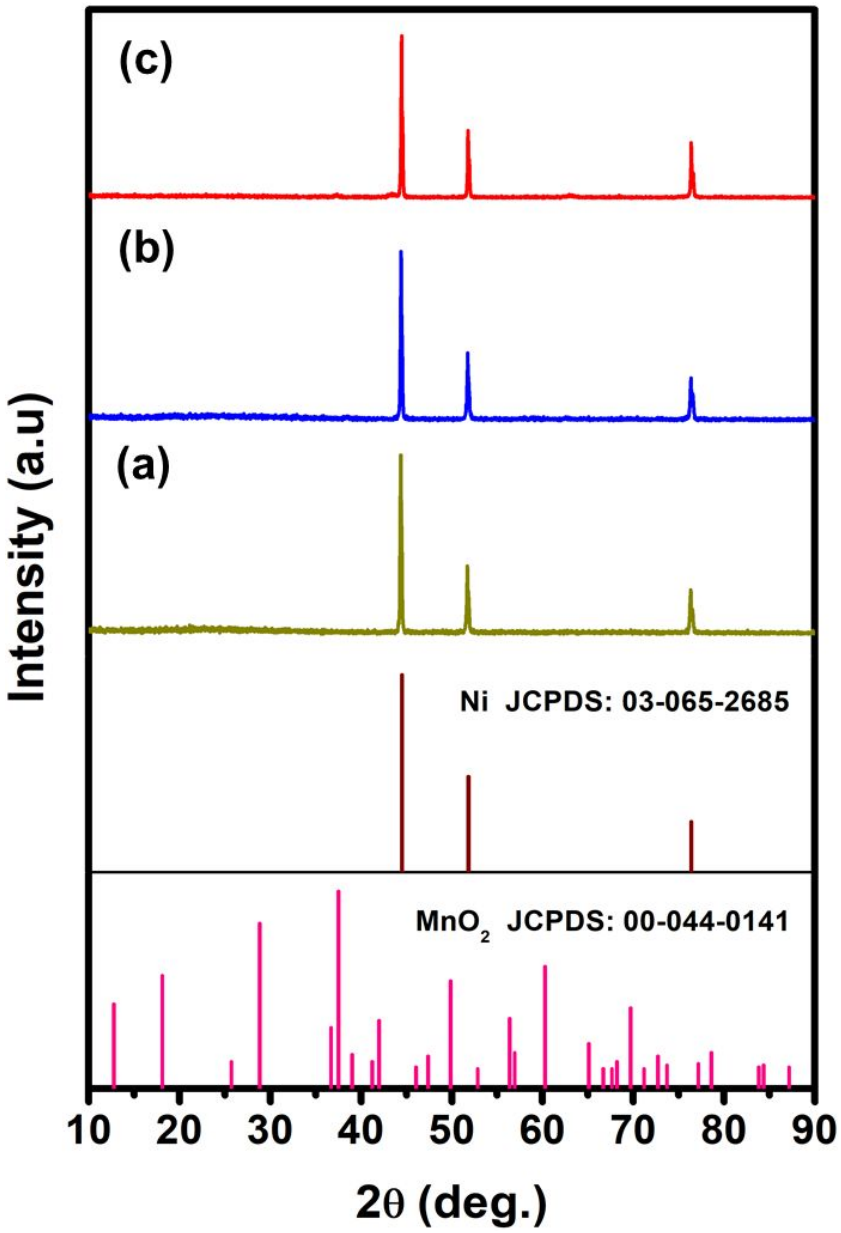

Figure S4. X-ray diffraction patterns of MnO_2 catalyst formed on Ni foam: (a) fresh Ni foam, (b) before annealing, and (c) after annealing at 450 °C for 5 h.

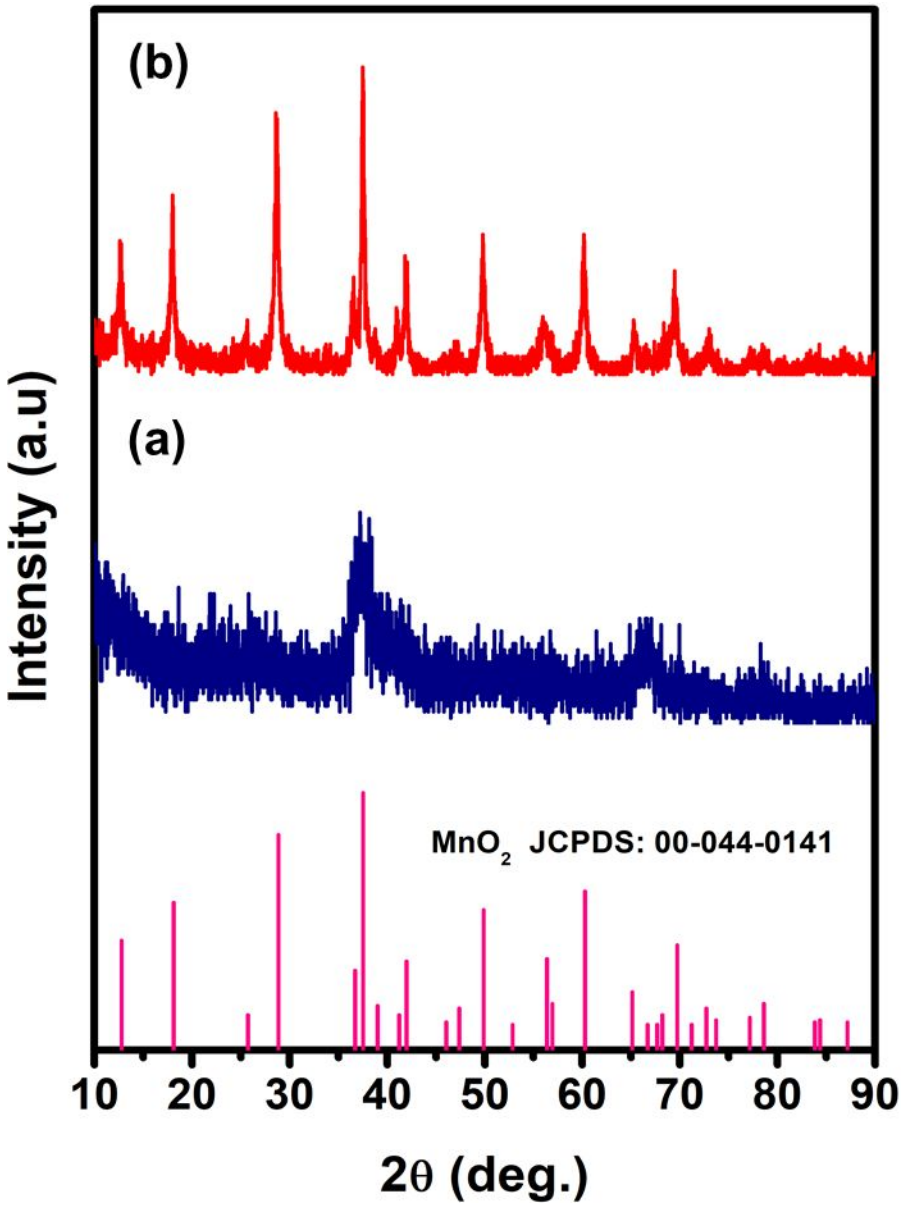

Figure S5. X-ray diffraction patterns of MnO_2 powder obtained via hydrothermal method:

(a) before annealing, and (b) after annealing at 450 °C for 5 h.

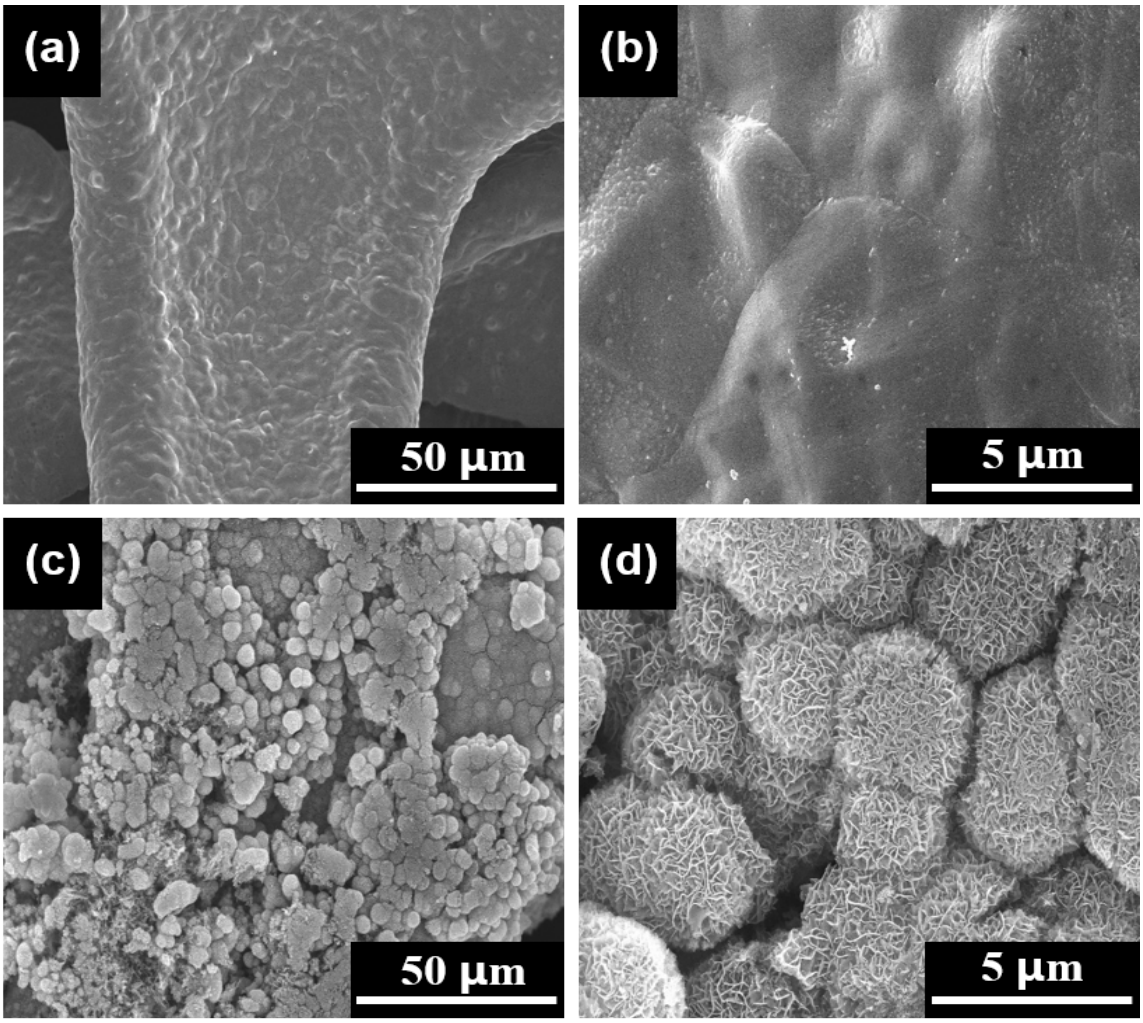

Figure S6. (a) Low- and (b) high-magnification scanning electron microscopy (SEM) images of fresh Ni foam. (c) Low- and (d) high-magnification SEM images of MnO_2 catalyst formed on Ni foam.

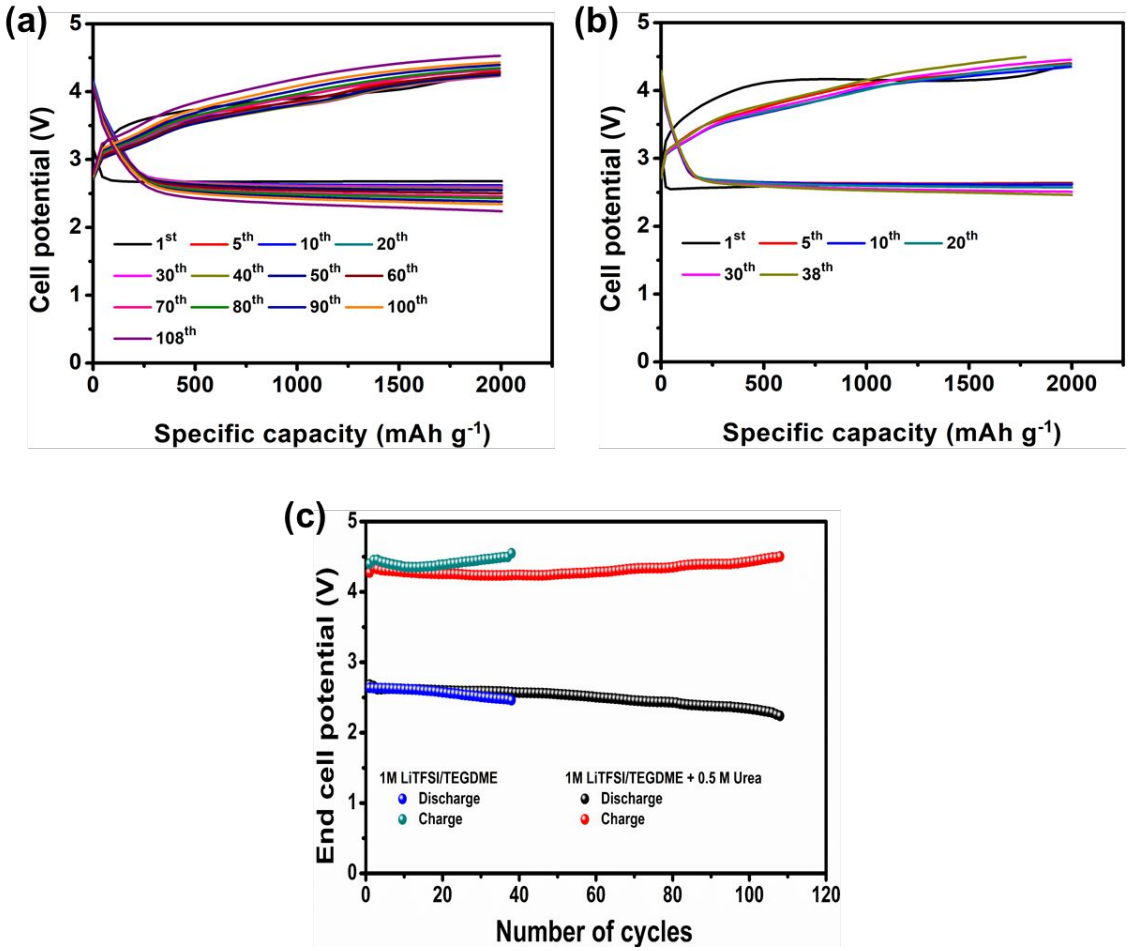

Figure S7. (a) and (b) Discharge–charge potential profiles of Li-O_2 batteries with and without urea additive. (c) Variation of end cell potential with cycle number of Li-O_2 batteries with and without urea electrolyte additive. Measurements were carried out in limited capacity mode: 2000 mAh g^{-1} and 0.2 mA cm^{-2} in pure O_2 atmosphere. Here,

LiTFSI and TEGDME denote bis(trifluoromethane sulfonyl)imide lithium salt and tetraethylene glycol dimethyl ether, respectively.