Electronic Supplementary Information

Lithium-Oxygen Batteries: Bridging Mechanistic Understanding and Battery Performance

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Calculations and assumptions of theoretical energy reported in Figure 1.

$q_{positive}$ [mAh/g]= gravimetric capacity of positive electrode

$q_{negative}$ [mAh/g] = gravimetric capacity of negative electrode

$V_{discharge}$ [V vs. negative] = discharge voltage of cell

$E_{positive}$ [Wh/kg] = energy density based on positive electrode weight = $q_{positive}V_{discharge}$

$E_{negative}$ [Wh/kg] = energy density based on negative electrode weight = $q_{negative}V_{discharge}$

$m^*_{negative,\ positive}$ = mass of negative or positive electrode required to give 1 Wh

$$E_{cell} = E_{negative+positive} = \frac{1}{m^*_{negative} + m^*_{positive}} = \frac{1}{\frac{1}{E_{negative}} + \frac{1}{E_{positive}}} [Wh/kg]$$

Gravimetric Energy

Positive Electrode	Negative Electrode	$V_{discharge}$ [V_{Li}]	$q_{negative}$ [mAh/g]	$q_{positive}$ [mAh/g]	$E_{negative}$ [Wh/kg]	$E_{positive}$ [Wh/kg]	E_{cell} [Wh/kg]
$LiFePO_4$	C_6 (no excess)	3.2	372	170	1190	544	*373*
$LiMn_2O_4$	C_6 (no excess)	3.7	372	148	1376	548	*392*
$LiCoO_2$	C_6 (no excess)	3.7	372	274	1376	1013	*584*
$LiCoO_2$ (delithiated)	Si (Lithiated to $Li_{15}Si_4$)	3.8	1857	295	7058	1120	*967*
S_8	Lithium (no excess)	2.2	3861	1672	8495	3678	*2567*

For calculation purposes, we have assumed $LiCoO_2$ as the positive electrode in the Si-$LiMO_2$ system in Figure 1 (main text).

Volumetric Energy

Bulk densities of $LiCoO_2$,[1] $LiFePO_4$,[1] $LiMn_2O_4$,[1] S[2] and $Li_{15}Si_4$[3] are obtained from references.

$E_{positive}$ [Wh/L] = energy density based on pos. electrode volume = $q_{positive}V_{discharge}\rho_{positive}$

$E_{negative}$ [Wh/L] = energy density based on neg. electrode volume = $q_{negative}V_{discharge}\rho_{negative}$

$V^*_{negative,\ positive}$ = volume of negative or positive electrode required to give 1 Wh

$$E_{cell} = E_{negative+positive} = \frac{1}{V^*_{negative} + V^*_{positive}} = \frac{1}{\frac{1}{E_{negative}} + \frac{1}{E_{positive}}} [Wh/L]$$

Positive Electrode	Negative Electrode	Negative Electrode Density [g/cm³]	Positive Electrode Density [g/cm³]	$E_{negative}$ [Wh/L]	$E_{positive}$ [Wh/L]	E_{cell} [Wh/L]
$LiFePO_4$	C_6 (no excess)	2.267	3.6	2698	1957	*1134*
$LiMn_2O_4$	C_6 (no excess)	2.267	4.2	3120	2303	*1325*
$LiCoO_2$	C_6 (no excess)	2.267	5.06	3120	5127	*1940*
$LiCoO_2$ (delithiated)	Si (Lithiated to $Li_{15}Si_4$)	1.179	5.06	8321	5667	*3371*
S_8	Lithium (no excess)	0.53	2.07	4502	7613	*2829*

In the case of a $LiCoO_2$ vs Si cell, there is a dramatic change in volume between the charged and discharged state. To accurately characterize the cell, we calculate the volumetric energy density of the cell in the charged state when the cell volume is highest. To do so, we assume the same density of $LiCoO_2$, but account for the increased (lithiated) volume of the silicon anode.

Calculations and assumptions of theoretical and reported energy reported in Figure 2.

Theoretical energy density of Li_2O_2

Theoretical capacity of Li_2O_2:

$$\rho^*_{Li2O2} = \frac{2 \cdot F}{M_{Li2O2} \cdot 3600 \frac{C}{Ah}} \cdot 1000 = 1168 \frac{mAh}{g_{Li2O2}}$$

F = 96485.3 C/mol
M_{Li2O2} = 45.881 g/mol

Assumed practical discharge voltage: V_{avg} = 2.75 V

Gravimetric energy:

$$E_{Li2O2} = V_{avg} \cdot \rho^*_{Li2O2} = 3212 \frac{Wh}{kg_{Li2O2}}$$

Energy and power of select[4-6] Li-O_2 cathodes on discharge (for references reporting total carbon loading)

m_C = carbon loading [mg]
m_{cat} = catalyst loading [mg] if present
q_C = gravimetric discharge capacity normalized to carbon [mAh/g_C]
i_C = gravimetric discharge current normalized to carbon [mA/g_C]
V_{avg} = estimated average discharge voltage [V_{Li}]

$$Q_{total} \equiv [mAh] = \text{total discharge capacity} = q_C \cdot m_C$$

$$q_{discharged} \equiv [mAh/g_{C+cat+Li2O2}] = \text{discharged electrode capacity} = \frac{Q_{total}}{m_C + m_{cat} + \frac{Q_{total}}{\rho^*_{Li2O2}}}$$

$$E_{discharged} = q_{discharged} V_{avg}$$

$$I_{total} \equiv [A] = \text{total discharge current} = i_C \cdot m_C$$

$$i_{discharged} = \frac{I_{total}}{m_C + m_{cat} + \frac{Q_{total}}{\rho^*_{Li2O2}}}$$

$$P_{discharged} = i_{discharged} V_{avg}$$

Reference	Electrode	V_{avg} [V_{Li}]	m_C [mg]	m_{cat} [mg]	q_C [mAh/g]	i_C [mA/g]	$E_{discharged}$ [Wh/kg]	$P_{discharged}$ [W/kg]
Freunberger et al., Angew. Chemie 2011 [4]	Super P carbon	2.5	1	0	2800	70	2060	52
Lee et al., EES 2012 [5]	Pristine $Na_{0.44}MnO_2$ nanowires	2.6	0.3	0.1	5700	70	2360	29
Wang et al., AFM 2012 [6]	Freestanding hierarchically porous carbon (graphene)	2.64	0.8	0	11060	280	2784	71
		2.6	0.8		6150	700	2551	290
		2.55	0.8		3060	1400	2155	986
		2.48	0.8		2020	2800	1835	2544

The energy and power of VC[7] and CNF[8] electrodes were obtained from the reported values, which were originally calculated using this approach.

Calculations and assumptions of theoretical energy reported in Figure 3.

Calculations are the same as for those of Figure 1 above, except an excess of Li (2x) is used:

$E_{negative}$ = energy density based on negative electrode weight = $q_{negative} V_{discharge}/2$

Gravimetric Energy

Positive Electrode	Negative Electrode	$V_{discharge}$ [V]	$q_{negative}$ [mAh/g]	$q_{positive}$ [mAh/g]	$E_{negative}$ [Wh/kg]	$E_{positive}$ [Wh/kg]	E_{cell} [Wh/kg]
$LiCoO_2$	Lithium (2x excess)	4	1931	274	7723	1095	*959*
$LiCoO_2$	C_6	3.7	372	274	1376	1013	*584*
Li_2O_2	Lithium (2x excess)	2.75	1931	1168	5309	3213	*2002*
Li_2O_2	C_6	2.45	372	1168	911	2863	*691*

Volumetric Energy

Bulk densities of $LiCoO_2$[1] and Li_2O_2[9] are assumed from references.

Positive Electrode	Negative Electrode	Negative Electrode Bulk Density [g/cm^3]	Positive Electrode Bulk Density [g/cm^3]	$E_{negative}$ [Wh/L]	$E_{positive}$ [Wh/L]	E_{cell} [Wh/L]
$LiCoO_2$	Lithium (2x excess)	0.53	5.06	4093	5543	*2354*
$LiCoO_2$	C_6	2.267	5.06	3120	5127	*1940*
Li_2O_2	Lithium (2x excess)	0.53	2.31	2814	7422	*2040*
Li_2O_2	C_6	2.267	2.31	2066	6613	*1574*

Supporting Figures

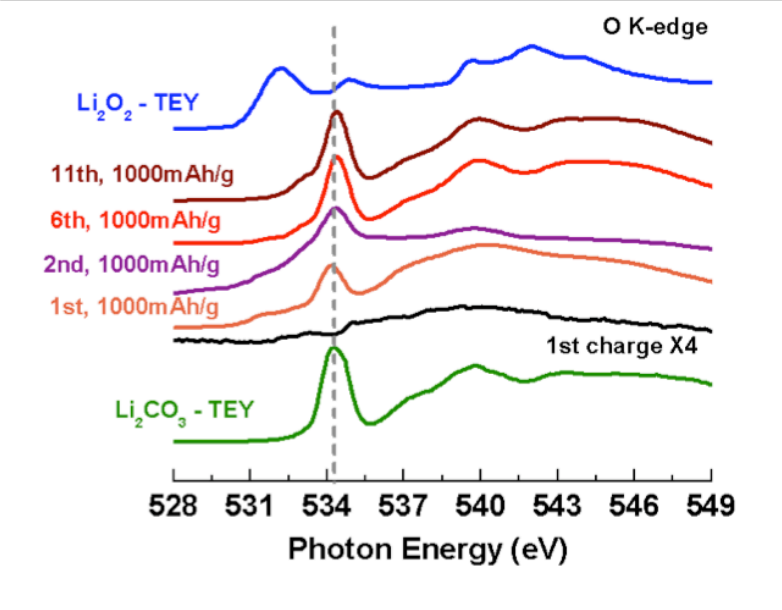

Figure S1. XANES TEY O K-edge data of VACNT electrodes cycled galvanostatically at 250 mA/g_C to a limited capacity of 1000 mAh/g_C and terminated on the indicated cycle number. The electrolyte was 0.1 M $LiClO_4$ in DME.

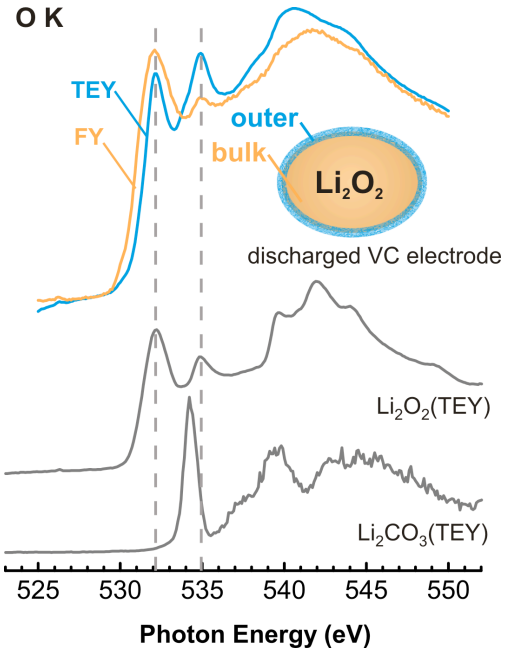

Figure S2. O K edge XANES TEY and FY spectra of a VC electrode discharged in 0.1 M $LiClO_4$ in DME at 100 mA/g_c to ~3000 mAh/g_c. Reference spectra (TEY) of Li_2O_2 (90%, Aldrich) and Li_2CO_3 (99%, Alfa Aesar) are included for comparison.

Figure S2 shows the oxygen K edge (O K) X-ray absorption near edge structure (XANES) spectra of the Li_2O_2 particles formed in a discharged VC electrode together with the reference spectra (TEY) of Li_2O_2 and Li_2CO_3 materials. Consistent with our recent report,[10] the XANES spectra of the discharged VC electrode resemble that of the Li_2O_2 reference material but not the Li_2CO_3 reference material. Interestingly, small differences were noted between the TEY and FY spectra of the Li_2O_2. The ratio of the peak intensity between the components at 532.0 eV and 534.9 eV increases from the TEY spectrum (probing the outer part of the Li_2O_2) to the FY spectrum (probing the bulk part of the Li_2O_2). This suggests that the stoichiometry and/or oxygen local environments are different between the outer part and the bulk part of the Li_2O_2, which can give rise to different charging behaviors at stage I (outer part) and stage II (bulk part). Further investigation including simulating XANES spectra with different "Li_2O_2" stoichiometry and/or defect structures is on going to reveal the physical origins responsible for these differences.

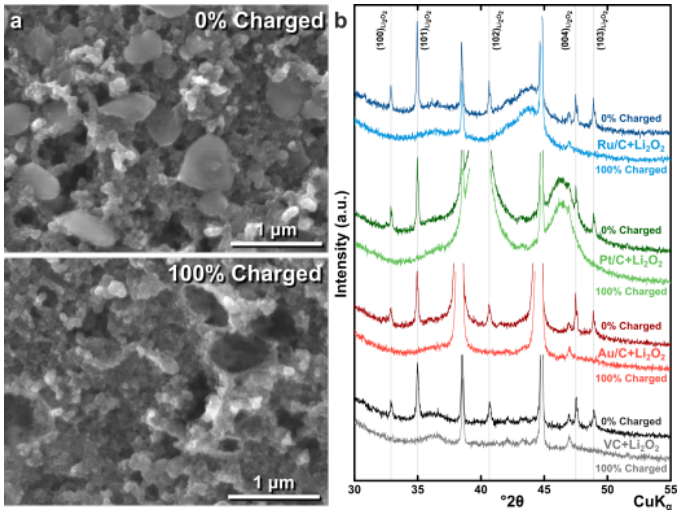

Figure S3: (a) SEM images of Li_2O_2-filled carbon electrode before charging (top) and after 100% charging (bottom); (b) XRD spectra of pristine and fully charged electrodes of Au/C- Li_2O_2, Pt/C- Li_2O_2 and Ru/C- Li_2O_2. All Li_2O_2 peaks are absent in the 100% charged electrodes. Adapted from Ref. [11]

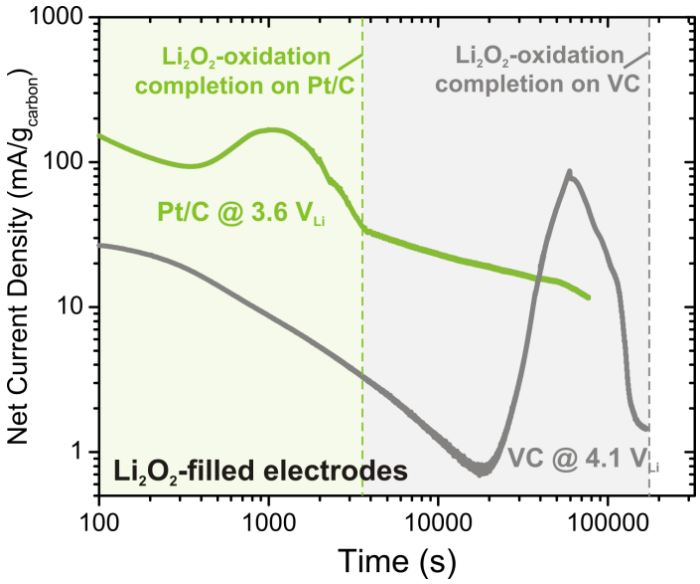

Figure S4: (a) SEM images of Li_2O_2-filled carbon electrode before charging (top) and after 100% charging (bottom); (b) XRD spectra of pristine and fully charged electrodes of Au/C- Li_2O_2, Pt/C- Li_2O_2 and Ru/C- Li_2O_2. All Li_2O_2 peaks are absent in the 100% charged electrodes. Adapted from Ref. [11]

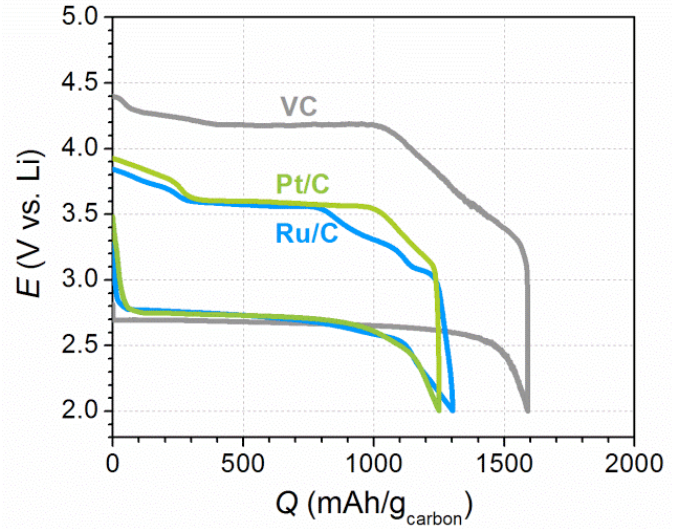

Figure S5: (a) Discharge and charge profiles of VC, Ru/C, and Pt/C in 0.1 M $LiClO_4$ in DME at 100 mA/g_c in Li-O_2 cells.

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