Supplementary Information for

# Thermal and Electrochemical Decomposition of Lithium Peroxide in Non-Catalyzed Carbon Cathodes for Li-Air Batteries

H. Beyer\*<sup>*a*</sup>, S. Meini<sup>*a*</sup>, N. Tsiouvaras<sup>*a*</sup>, M. Piana<sup>*a*</sup>, and H. A. Gasteiger<sup>*a*</sup>

<sup>a</sup> Institute of Technical Electrochemistry, Technische Universität München, Lichtenbergstr. 4, D-85748, Garching, Germany. Fax: +498928913674; Tel: +4 8928913658; E-mail: hans.beyer@tum.de

### Electrochemical oxidation of Li2O2 in prefilled electrodes using an LFP counterelectrode

To calculate the extent of oxygen consumption at the Li metal anode under the experimental conditions in Fig. 3 of the manuscript, a charging experiment of an identical  $Li_2O_2$ -prefilled cathode under the same conditions, but using a LFP anode and an additional solid electrolyte diffusion barrier (Ohara glass) is conducted (s. Fig. S1).



**Fig. S1** Galvanostatic charging of a Li<sub>2</sub>O<sub>2</sub>-prefilled electrode (Li<sub>2</sub>O<sub>2</sub>/PEO/C) with 0.39 mg<sub>carbon</sub>/cm<sup>2</sup>) under argon at 120 mA/g<sub>carbon</sub> ( $\equiv$ 83 µA) in DEGDME with 0.2 M LiTFSI using an LFP counterelectrode and a solid electrolyte diffusion barrier (Ohara glass): *i*) red line: galvanostatic voltage profile; *ii*) blue line: current-normalized molar gas evolution rate of O<sub>2</sub>. The dotted blue line shows the theoretical O<sub>2</sub> evolution rate corresponding to the desired oxygen evolution rate of 2e<sup>-</sup>/O<sub>2</sub> (according to Eq. 1 in the main manuscript); the vertical dashed gray line marks the theoretical charging capacity of 1110 mAh/g<sub>carbon</sub> (based on a Li<sub>2</sub>O<sub>2</sub>/C weight ratio of 1/1 and 95% Li<sub>2</sub>O<sub>2</sub> purity).

It is found that the average  $O_2$  evolution rate in Fig. S1 corresponds to  $\approx 4.70 \,\mu$ mol/(As). Comparing this rate to the average  $O_2$  evolution rate of  $\approx 4.45 \,\mu$ mol/(As) obtained in Fig. 3 of the manuscript, the oxygen consumption at the lithium anode in Fig. 3 equals  $\approx 0.25 \,\mu$ mol/(As). This finding implies that the remaining discrepancy between the oxygen evolution in Fig. S1 and the theoretical oxygen evolution rate of 5.18  $\mu$ mol/(As) has to be due to other side reactions, as further discussed in the manuscript.

#### TA of carbon (Vulcan XC72)



Fig. S2 TGA (sample mass vs. temperature) and on-line MS of evolved gases (mass traces with m/z of 28, and 44 attributed to CO, and CO<sub>2</sub>, respectively) of carbon (Vulcan XC72). The percentage value given next to the TGA curve represents the measured mass loss,  $\Delta m$  meas, of the observed transition. The sample was ramped from 25 to 925°C in 67% O<sub>2</sub>/Ar at a heating rate of 10 K/min.

The onset temperature of the thermal oxidation of carbon in  $67\%O_2/Ar$  is  $500^\circ$ C, as seen in Fig. S2. The oxidation product is CO<sub>2</sub> (as the intensities of the m/z 28 and 44 traces reflect the fingerprint ionization pattern of CO<sub>2</sub>). The quantitative gasification of carbon is complete at  $700^\circ$ C.

## TA of PEO/C

To better understand the TA of  $Li_2O_2$ /PEO/C electrodes, it is important to determine the reactions of a PEO/C mixture and the evolved gases during the same procedure that is used for the TA of electrodes. Thus, a PEO/C sample is first heated from 25 to 925°C in Ar, then held isothermal at 925°C while the atmosphere is switched from Ar to 67vol.% O<sub>2</sub> in Ar (s. Fig. S3).



**Fig. S3** TGA (sample mass vs. temperature) and on-line MS of evolved gases (mass traces with m/z of 32, 18, 28, 44, 15, and 88 attributed to  $O_2$ ,  $H_2O$ , CO,  $CO_2$ ,  $CH_3$ , and  $C_4H_8O_2$ , respectively) of C/PEO (mixing ratio 2/0.2). The percentage values given next to the TGA curve represent the measured mass losses,  $\Delta m$  meas, for each of the observed transitions. The multipliers/divisors in the mass trace labels represent the amplification factors used on the relative intensities of the respective signals. The sample was ramped at 10 K/min from 25 to 925°C in Ar and subsequently held isothermal at 925°C in 67vol.%  $O_2/Ar$ .

In the temperature range of roughly 300 to 450°C, PEO is decomposed quantitatively to volatile products (9.0% measured weight loss compared to 9.1% PEO content). Besides water and trace amounts of CO, also methyl- and/or dimethyl ether fragments (identified by the m/z 15 trace, which is also observed during the anodic oxidation of the chemically very similar DEGDME electrolyte shown in Fig. 2 of the manuscript) and 1,4-dioxane (generally accepted as the parent molecule of the m/z 88 trace)<sup>1</sup> are detected by the MS. The overall reaction is described in the manuscript, Tab. 3, reaction N°9. In Section 3.5 of the manuscript, the m/z 15 trace is chosen to monitor the decomposition of PEO to volatile organic fragments. Regarding the temperature range of PEO decomposition, it is expected to interfere with other processes in the thermal analysis of prefilled electrodes. The carbon fraction of the sample does not react up to 925°C under argon. When the atmosphere is switched to 67vol.% O<sub>2</sub> in Ar at 925°C, the total oxidation of carbon occurs, releasing CO<sub>2</sub> (the m/z 28 trace gives a signal ~1/9 of the intensity of the m/z 44 trace, which is consistent with the fingerprint of pure CO<sub>2</sub>). Accordingly, no residue of the PEO/C sample is left at the end of the analysis.

### TA of Li<sub>2</sub>CO<sub>3</sub>/C



**Fig. S4** TGA (sample mass vs. temperature) and on-line MS of evolved gases (mass traces with m/z of 32, 28, and 44 attributed to  $O_2$ , CO, and  $CO_2$ , respectively) of Li<sub>2</sub>CO<sub>3</sub>/C (mixing ratio 1/1). The percentage values given next to the TGA curve represent the measured mass losses,  $\Delta m$  meas, for each of the observed transitions. The multipliers/divisors in the mass trace labels represent the amplification factors used on the relative intensities of the respective signals. The sample was ramped from 25 to 925°C in Ar at a heating rate of 10 K/min and subsequently held isothermal at 925°C in 67vol.% O<sub>2</sub>/Ar.

Fig. S4 shows that the presence of carbon changes both the temperature window and the reaction mechanism of  $Li_2CO_3$  decomposition. Between 650 and 900°C,  $Li_2CO_3$  reacts with carbon to form  $Li_2O$  and CO. The measured mass loss of 38.0% corresponds very well to the calculated loss of 37.9% for reaction N°14 (Tab. S1).

Table S1 Reactions of a Li2CO3/C m	ixture (mixing ratio 1/1) obs	served during thermal analysis.
------------------------------------	-------------------------------	---------------------------------

N°	T range [°C]	atmos- phere	reaction	∆m(total) theo./meas. [% sample]	∆m(LiX) theo./meas. [% sample]	∆m(C) theo./meas. [% sample]	evolved(†) gases	$\Delta G_R at T_{onset}/T_{endset}$ [kJ/mol]
(14)	650–900	Ar	$Li_2CO_3 + C \rightarrow Li_2O + 2 CO$	-37.9 / -38.0	-29.8 / -29.9	-8.1 / -8.1	CO↑	+84/-2
(6)	925	$O_2$	$C + O_2 \rightarrow CO_2$	-41.9 / -39.5	0 / 0	-41.9 / -39.5	$\mathrm{CO}_2\uparrow$	-387

### TA of LiOH/C



**Fig. S5** TGA (sample mass vs. temperature) and on-line MS of evolved gases (mass traces with m/z of 32, 18, 28, 44, and 2 attributed to  $O_2$ ,  $H_2O$ , CO, CO<sub>2</sub>, and  $H_2$ , respectively) of LiOH/C (mixing ratio 1/1). The percentage values given next to the TGA curve represent the measured mass losses,  $\Delta m$  meas, for each of the observed transitions. The multipliers/divisors in the mass trace labels represent the amplification factors used on the relative intensities of the respective signals. The sample was ramped from 25 to 925°C in Ar at a heating rate of 10 K/min and subsequently held isothermal at 925°C in 67vol.%  $O_2/Ar$ .

The MS traces in Fig. S5 point out that the mass loss between 400 and 620°C arises from two distinct reactions: The decomposition of LiOH without the involvement of carbon (Tab. S2, N°3) produces  $H_2O$ , whereas the simultaneous reaction of LiOH with carbon (Tab. S2, N°13) releases  $H_2$ . Both reactions produce  $Li_2O$ , and reaction N°13 additionally yields  $Li_2CO_3$ , which subsequently decomposes between 650 and 900°C following the same mechanism as discussed for  $Li_2CO_3/C$  mixtures. The measured weight loss of 23.2 % during  $Li_2CO_3$  decomposition indicates a transient  $Li_2CO_3$  content of 29.7 wt.% in the sample. This number suggests that initially, 11.2 wt.% of the sample mass (=22.4 % of LiOH) react via N°3, whereas 38.8 wt.% (=77.6 % of LiOH) react via N°13. This ratio would theoretically arise from a weight loss of 5.8 % between 400 and 650°C (4.2 % from N°3 and 1.6 % from N°13), which exactly matches the actually measured value.

Table S2 Reactions of a LiOH/C mixture (mixing ratio 1/1) observed during thermal analysis.

N°	T range [°C]	atmos- phere	reaction	∆m(total) theo./meas. [% sample]	∆m(LiX) theo./meas. [% sample]	∆m(C) theo./meas. [% sample]	evolved(†) gases	$\Delta G_R at T_{onset}/T_{endset}$ [kJ/mol]
(3)	400–650	Ar	$2 \ {\rm LiOH} \rightarrow {\rm Li_2O} + {\rm H_2O}$	-18.8 / -4.2	-18.8 / -4.2	0 / 0	$\mathrm{H_2O}\!\!\uparrow$	+42 / +10
(13)	400–650	Ar	$\begin{array}{l} 4 \ LiOH + C \rightarrow Li_2CO_3 + Li_2O \\ & + 2 \ H_2 \end{array}$	-2.1 / -1.6	+4.2 / +3.3	-6.3 / -4.9	${ m H_2}\uparrow$	-8 / -62
(14)	650–850	Ar	$Li_2CO_3 + C \rightarrow Li_2O + 2 CO$	var. / -23.2	-17.7 / -18.2	-4.8 / -5.0	CO↑	+84 / ±15
(6)	925	$O_2$	$C + O_2 \rightarrow CO_2$	-38.9 / -38.2	0 / 0	-38.9 / -38.2	$\mathrm{CO}_2\uparrow$	-387

## Thermodynamic data of lithium salts

**Table S3** Data used for all thermodynamic calculations in this work.  $G_{(T_0)}$ ,  $S_{(T_0)}$  and  $c_{p_{(T_0)}}$  values are generally taken from<sup>2</sup>, except for  $c_{p_{(T_0)}}$  of Li<sub>2</sub>O<sub>2</sub>, as discussed in Section 3.3.

compound	$\Delta H^f_{(T_0)}$ [kJ/mol]	$\Delta G^{f}_{(T_0)}$ [kJ/mol]	S <sub>(T0)</sub> [J/(molK)]	С <sub>р(Т0)</sub> [J/(molK)]
Li (s)	0	0	29.1	24.8
<b>C</b> (s)	0	0	5.7	8.5
$\mathbf{H}_{2}\left(\mathbf{g} ight)$	0	0	130.7	28.8
$O_{2}\left(g ight)$	0	0	205.2	29.4
CO (g)	-110.5	-137.2	197.7	29.1
$CO_{2}\left(g ight)$	-393.5	-394.4	213.8	37.1
$H_2O\left(g\right)$	-241.8	-228.6	188.8	33.6
$Li_2O(s)$	-597.9	-561.2	37.6	54.1
$Li_{2}O_{2}\left(s ight)$	-634.3	-570.2	56.42	71.0
LiOH (s)	-487.5	-441.5	42.8	49.6
$Li_{2}CO_{3}\left(s\right)$	-1215.9	-1132.1	90.4	99.1

## Literature

- 1 G. K. Jones, A. R. McGhie, and G. C. Farrington, *Macromolecules*, 1991, 24, 3285–3290.
- 2 D. R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 85th ed., CRC Press, Boca Raton, FL, 2004–2005, pp. 5-4 5-60.