

**Supplementary Information**

for

**Rechargeability of Li-air cathodes pre-filled with discharge products using an  
ether-based electrolyte solution: implications for cycle-life of Li-air cells.**

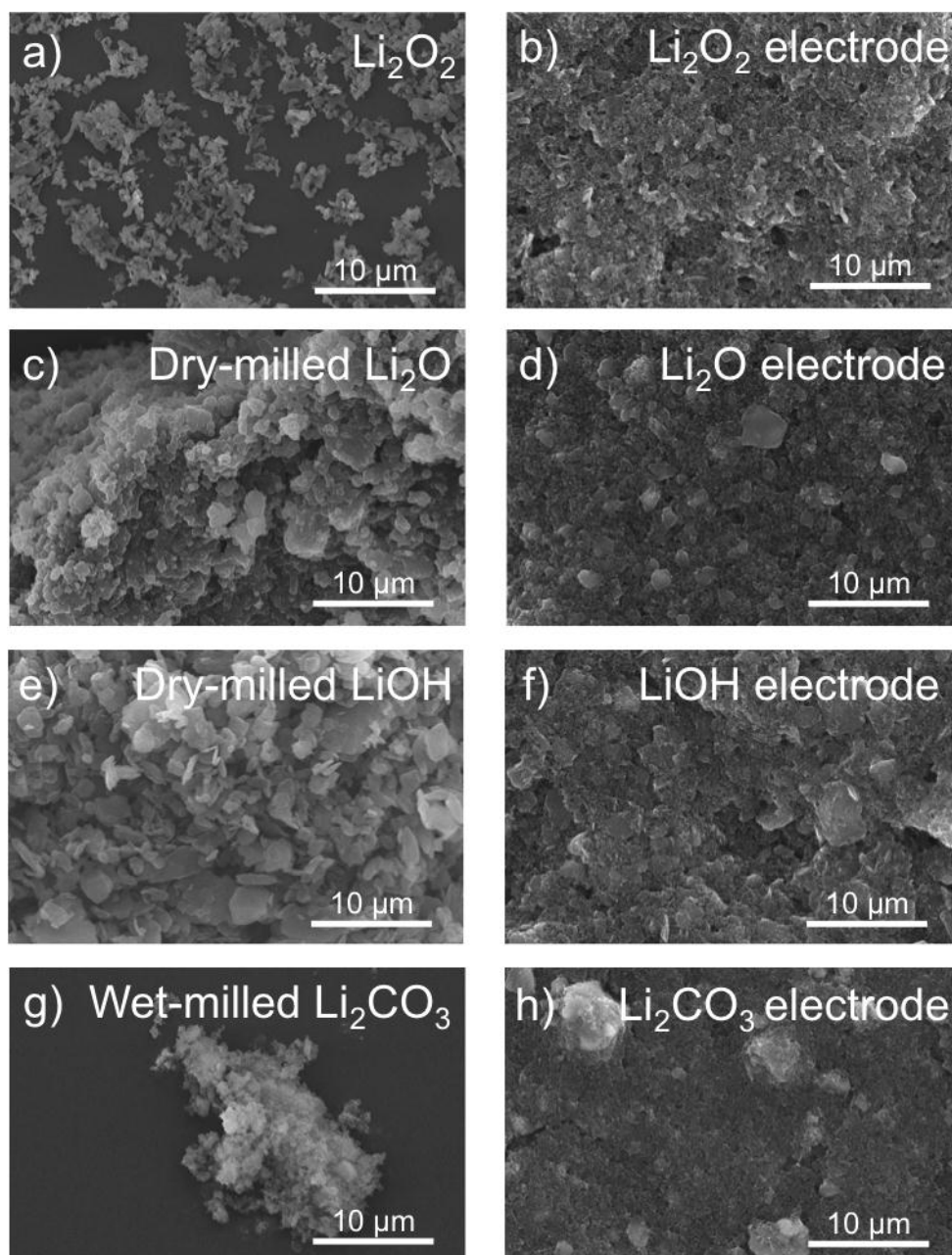
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### **Ball-milling of active materials powders and SEM investigation of final electrodes (non-catalyzed carbon).**

LiOH, Li<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>O powders were ball-milled prior to electrode preparation to reduce particle size. In order to avoid parasitic reactions and thus contamination of the electrodes, LiOH and Li<sub>2</sub>O were ball-milled without solvent using 3 mm Ø ZrO<sub>2</sub> balls at 700 rpm in dry Ar atmosphere for one hour (Pulverisette 7 planetary ball-mill, Fritsch, Germany); the material/balls ratio was always 1/6 g/g. Using this procedure (Figure S1 shows Li<sub>2</sub>O and LiOH ball-milled powders), it was indeed possible to obtain a uniform distribution of the active material in the electrode matrix for both LiOH and Li<sub>2</sub>O powders and only ≈1 μm particles of LiOH and Li<sub>2</sub>O are observed by SEM in the respective electrodes; apparently, agglomerates > 1 μm are mostly dispersed during sonication.

Due to its chemical stability, making parasitic reactions with most solvents highly unlikely, Li<sub>2</sub>CO<sub>3</sub> was wet-milled in NMP in order to try to obtain even smaller particles. A 2/3 g/g suspension of Li<sub>2</sub>CO<sub>3</sub> in NMP (Aldrich, anhydrous, 99.5 %) was ball-milled for one hour at 700 rpm with 3 mm Ø diameter ZrO<sub>2</sub> balls. The Li<sub>2</sub>CO<sub>3</sub>/balls ratio was ≈1/5 g/g. Despite the quite smaller primary particles of wet-milled Li<sub>2</sub>CO<sub>3</sub> compared to, for instance, dry milled LiOH (compare Figure S1 e) and g), agglomeration seems to occur during ink sonication since relatively large agglomerates (up to several micrometer) can be observed in the electrodes by SEM. Nevertheless, the differences in terms of particle size and distribution between Li<sub>2</sub>CO<sub>3</sub>, LiOH, and Li<sub>2</sub>O pre-filled electrodes are relatively minor, and we therefore expect comparable electrical contact between the active materials and the carbon support.



**Figure S1:** SEM micrographs of active material and final pre-filled electrodes based on Vulcan carbon and PEO binder: a)  $\text{Li}_2\text{O}_2$  as received; b)  $\text{Li}_2\text{O}_2$  final electrode; c) dry-milled  $\text{Li}_2\text{O}$  sample; d)  $\text{Li}_2\text{O}$  final electrode; e) dry-milled  $\text{LiOH}$  sample; and, f)  $\text{LiOH}$  final electrode; g) wet-milled  $\text{Li}_2\text{CO}_3$  sample; and, h)  $\text{Li}_2\text{CO}_3$  final electrode