

## Supporting Information for

# Novel approach for high-energy-density Li-air battery: tri-dimensional growth of $\text{Li}_2\text{O}_2$ crystals tailored by $\text{Li}^+$ ion concentrations

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**Table S1.** Average granule diameters and discharge capacities in electrolytes with the concentration of LiTFSI in TEGDME varied from  $10^{-3}$  M to 5 M.

Li <sup>+</sup> (mol L <sup>-1</sup> )	$10^{-3}$	$10^{-2}$	$10^{-1}$	1	2	3	4	5
Average granule diameter (nm)	86.3	139.2	394.4	549.9	5417.7	5824.8	111.3	414.4
Discharge capacity (mA h g <sub>carbon</sub> <sup>-1</sup> )	2211	3013	6055	7529	12250	13245	2461	3967

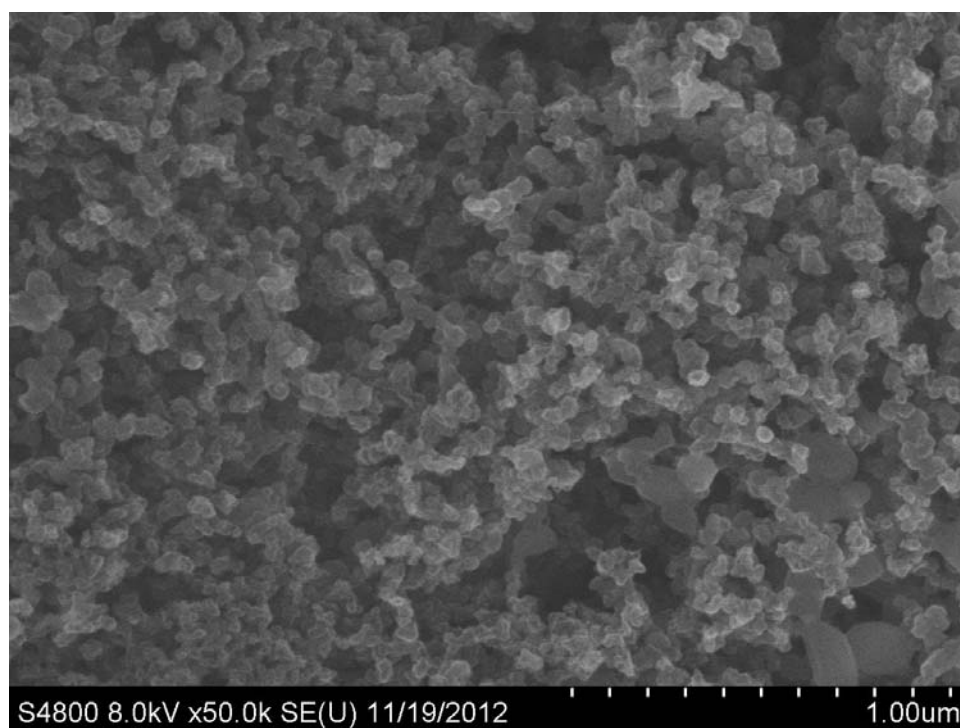
**Table S2.** Average granule diameters and thicknesses of product belts of the cathodes obtained at controlled discharge capacities in electrolytes with 3 M Li<sup>+</sup> ion.

Discharge capacity (mA h g <sub>carbon</sub> <sup>-1</sup> )	0	3000	5000	7000	9000	13245
Average granule diameter (nm)	63.9	85.1	394.8	549.7	5417.5	5824.8
Average thickness of product belt (nm)				32.6	48.2	79.6

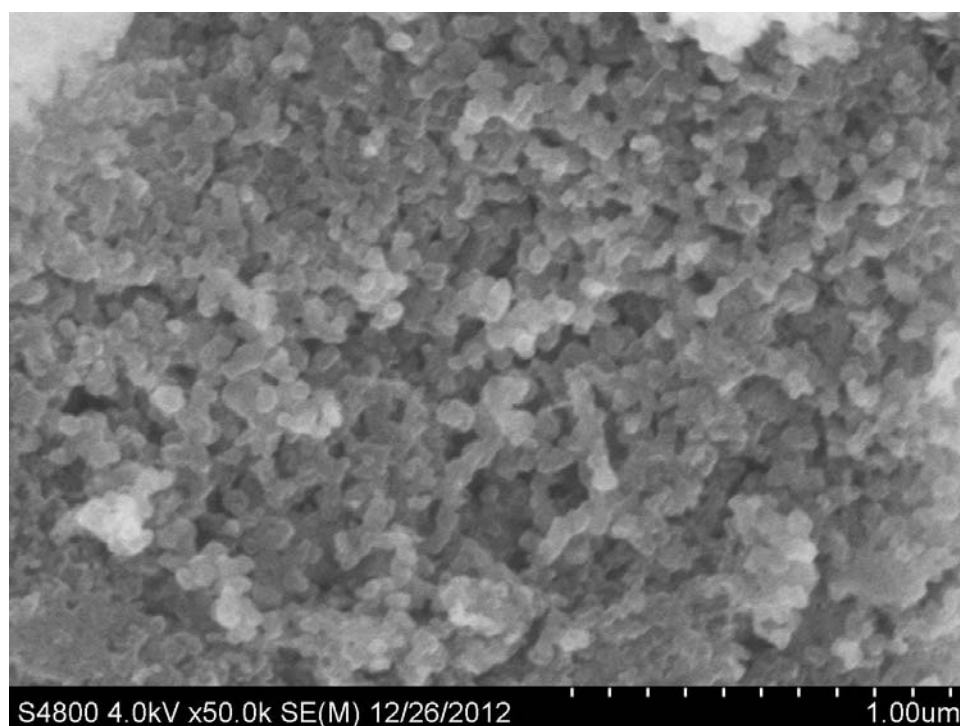
**Figure S1.** Home-made Li-air test system, based on Etelux glove box, filled with  $N_2+O_2$  (78:22, v/v) and humidity is controlled less than 1 ppm.



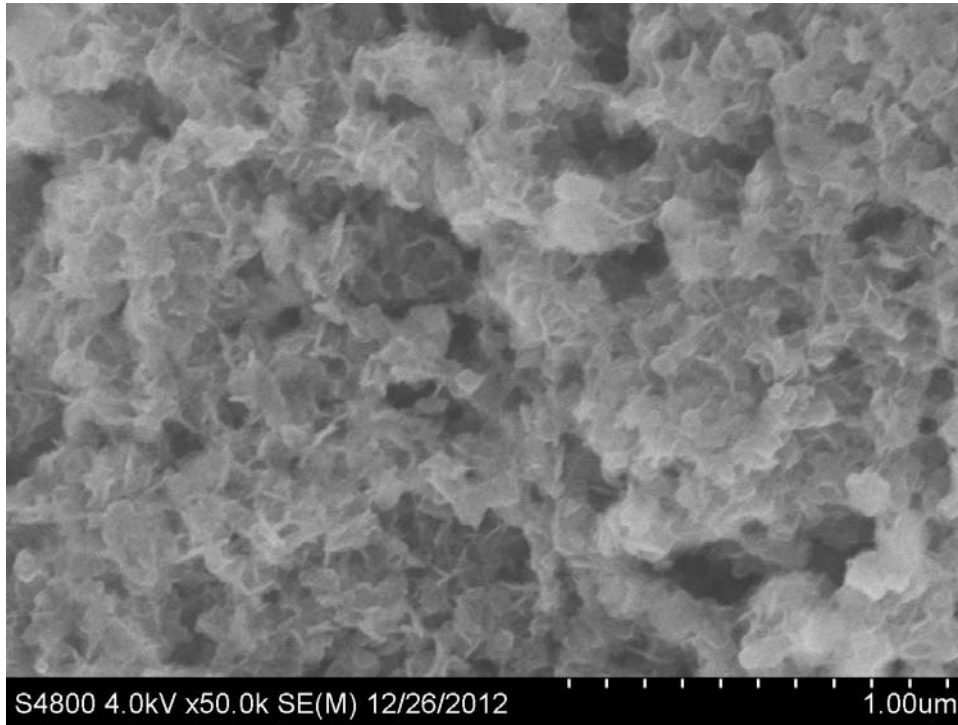
**Figure S2.** Full size SEM images of the cathode surfaces before and after discharge.



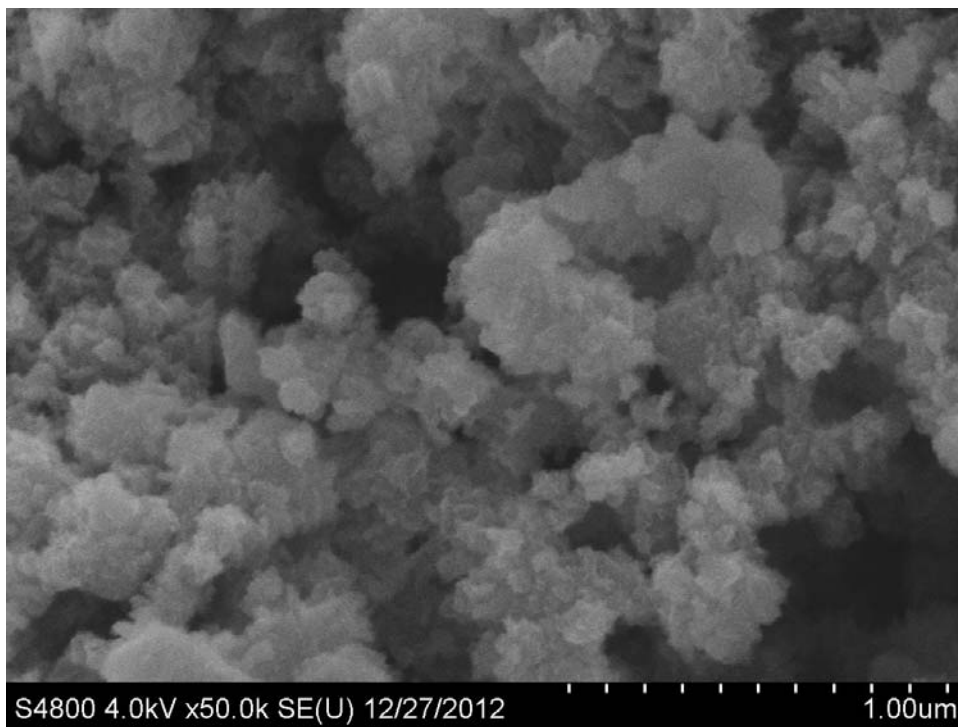
a) Full size SEM image of pristine cathode surface.



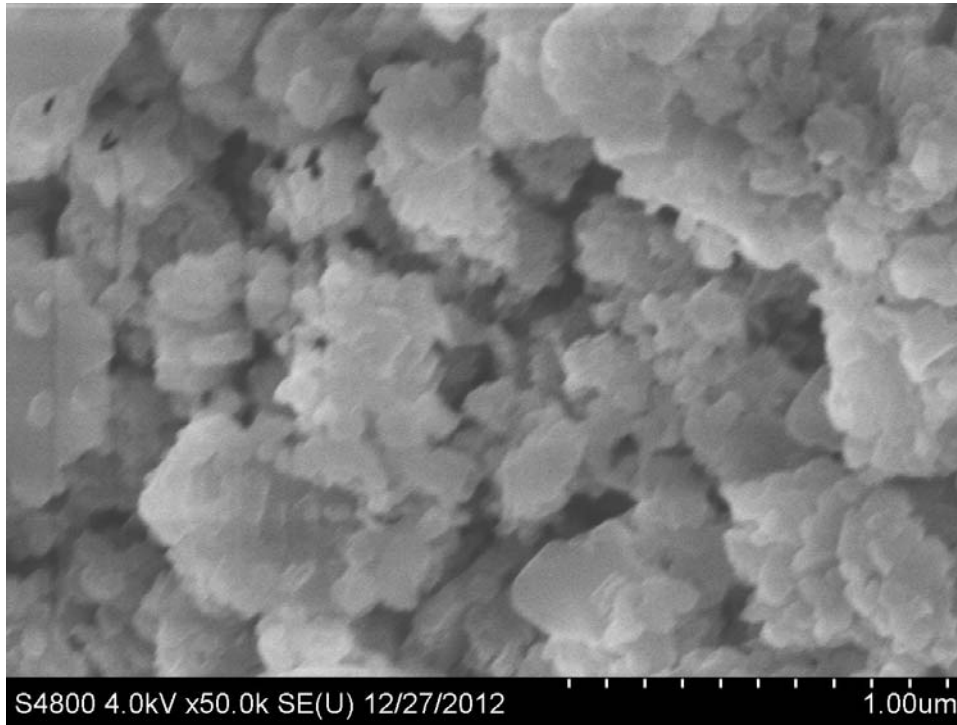
b) Full size SEM image of the cathode surface after discharge in the  $10^{-3}$  M electrolyte.



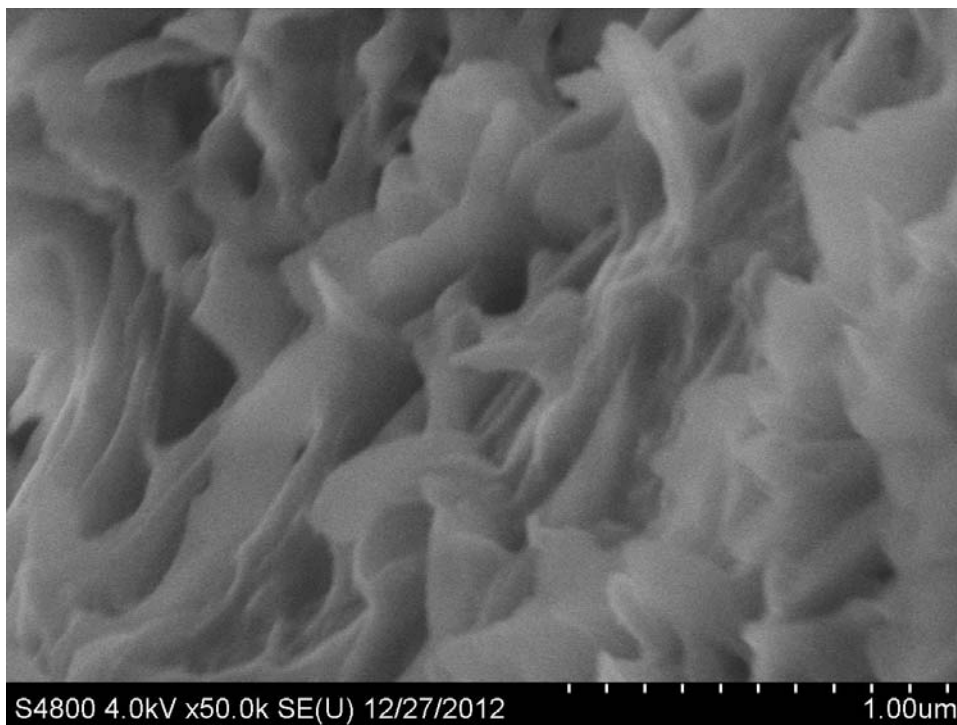
c) Full size SEM image of the cathode surface after discharge in the  $10^{-2}$  M electrolyte.



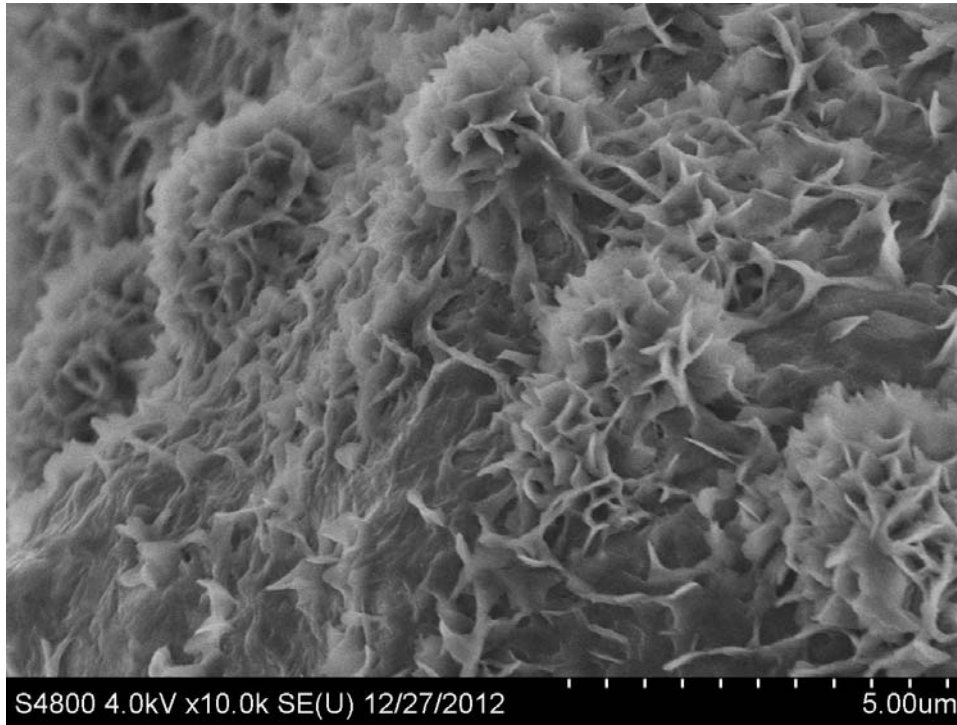
d) Full size SEM image of the cathode surface after discharge in the  $10^{-1}$  M electrolyte.



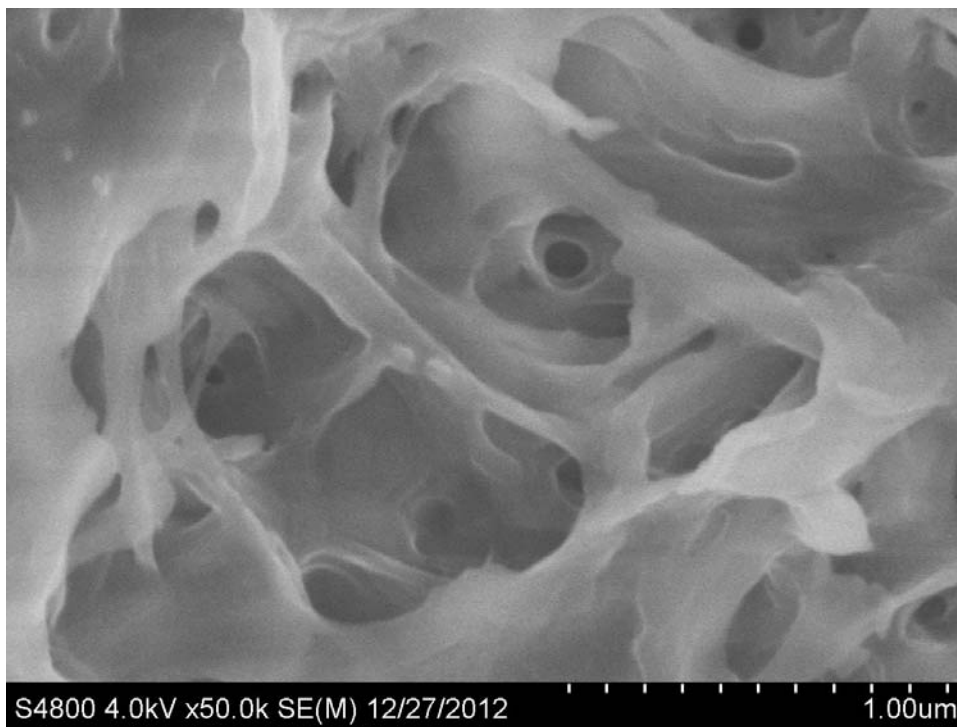
e) Full size SEM image of the cathode surface after discharge in the 1 M electrolyte.



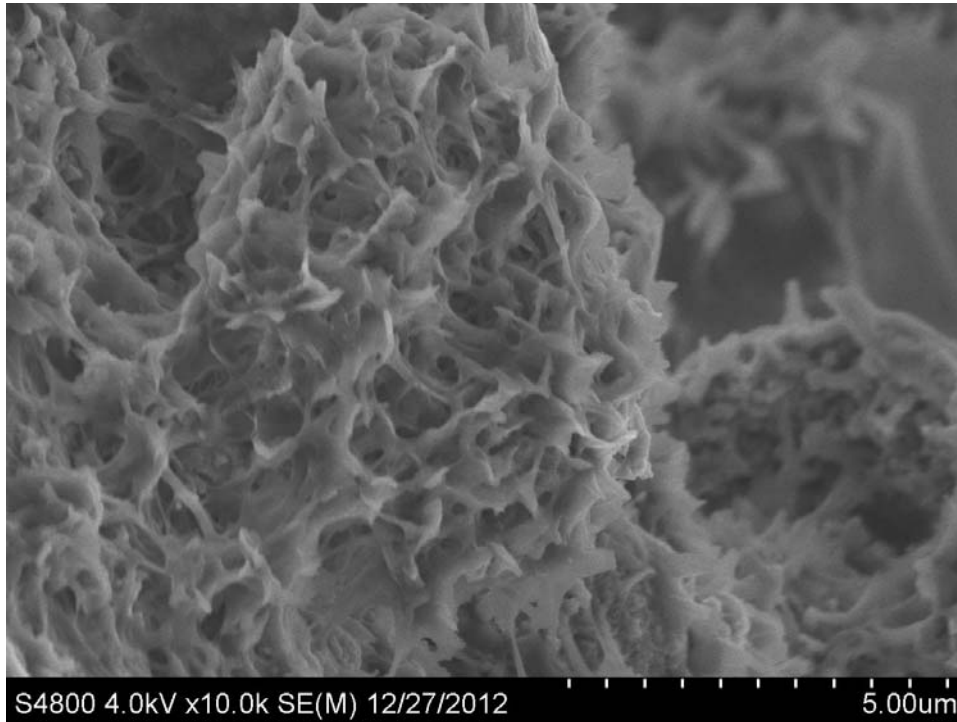
f) Full size SEM image1 of the cathode surface after discharge in the 2 M electrolyte.



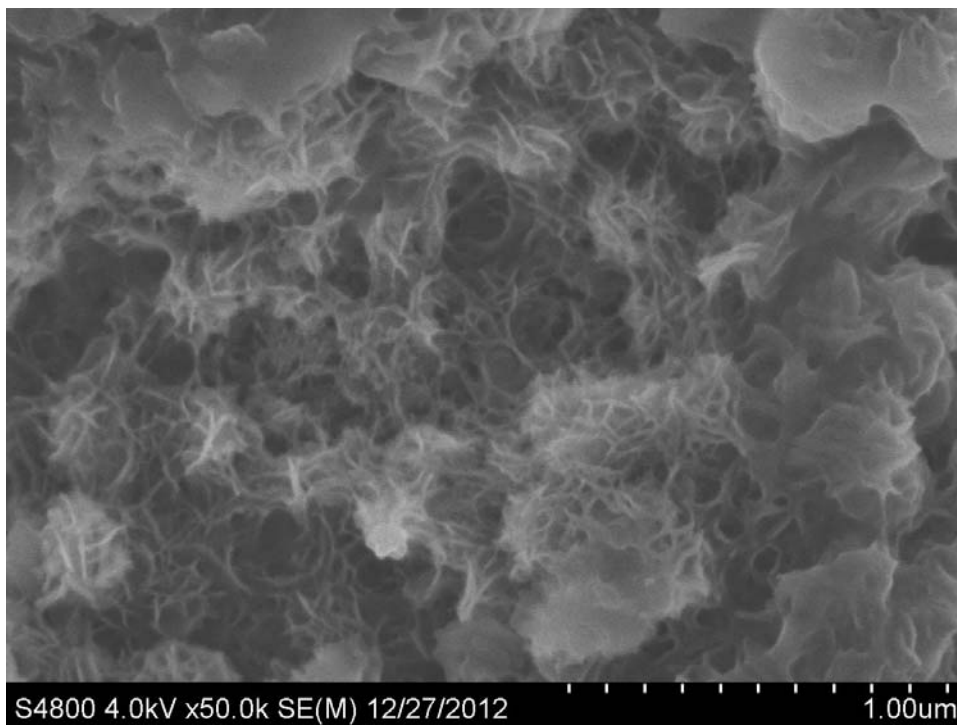
g) Full size SEM image2 of the cathode surface after discharge in the 2 M electrolyte.



h) Full size SEM image1 of the cathode surface after discharge in the 3 M electrolyte.

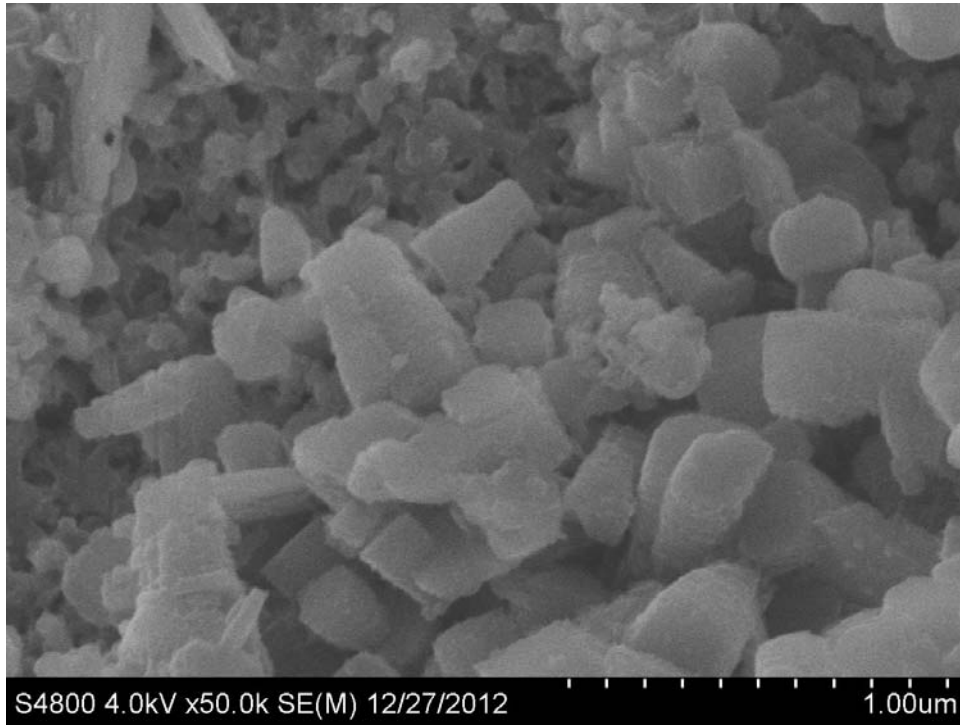


i) Full size SEM image2 of the cathode surface after discharge in the 3 M electrolyte.



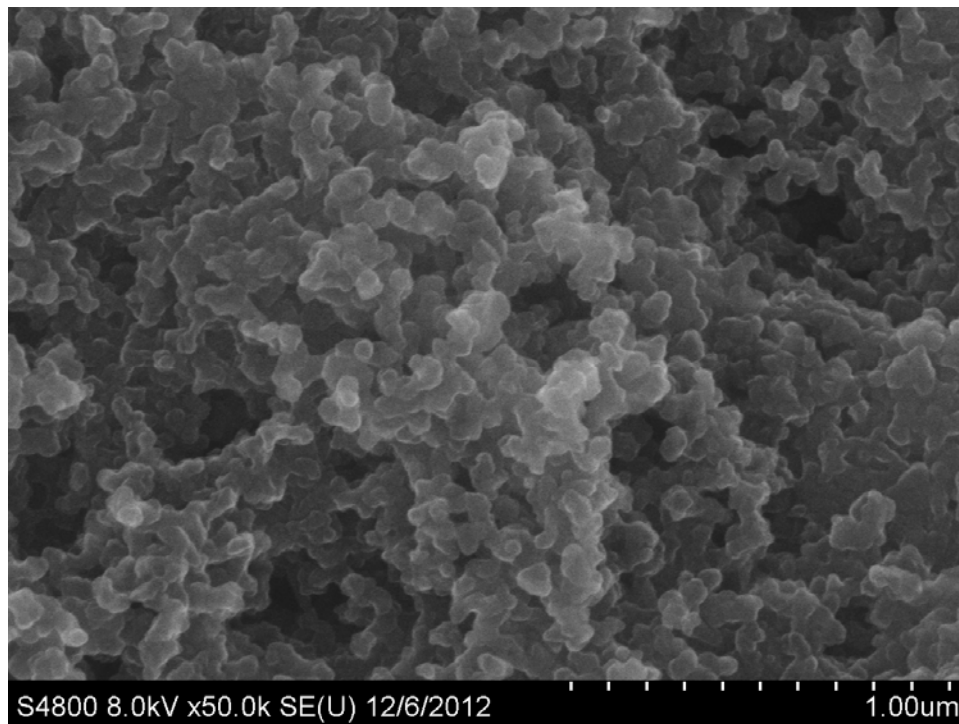
j) Full size SEM image of the cathode surface after discharge in the 4 M electrolyte.



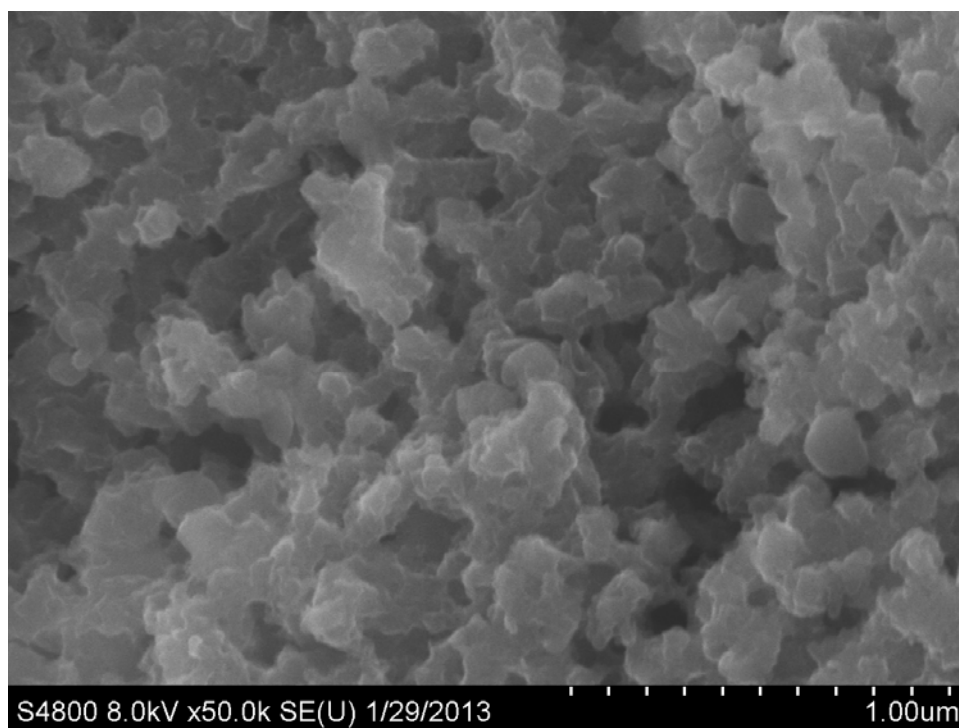


k) Full size SEM image of the cathode surface after discharge in the 5 M electrolyte.

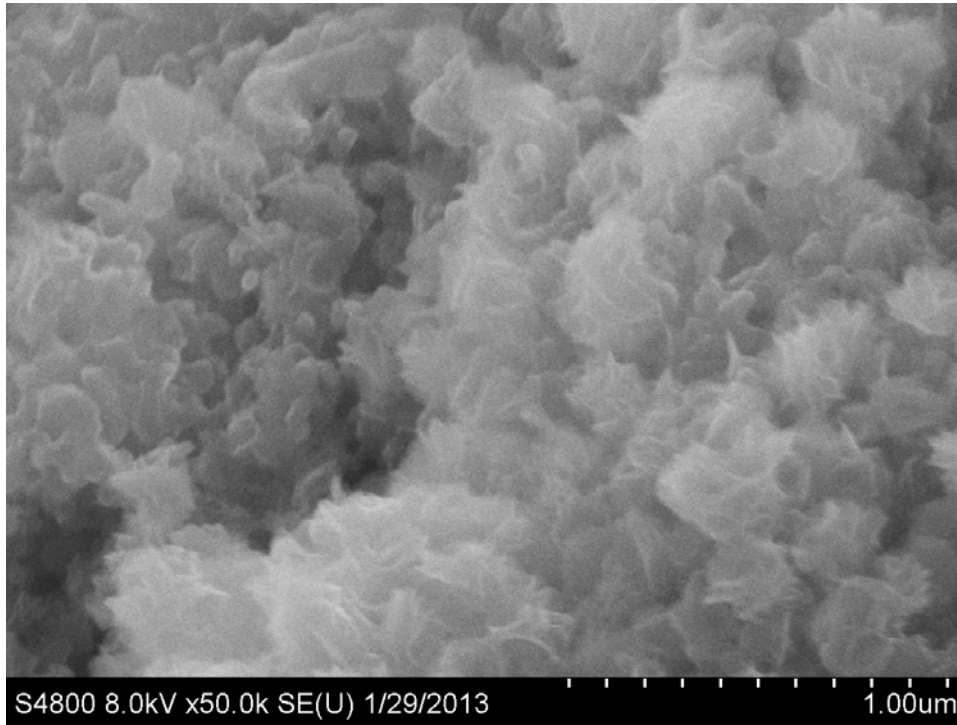
**Figure S3.** Full size SEM images of the cathode surfaces at controlled discharge capacities in 3 M electrolyte.



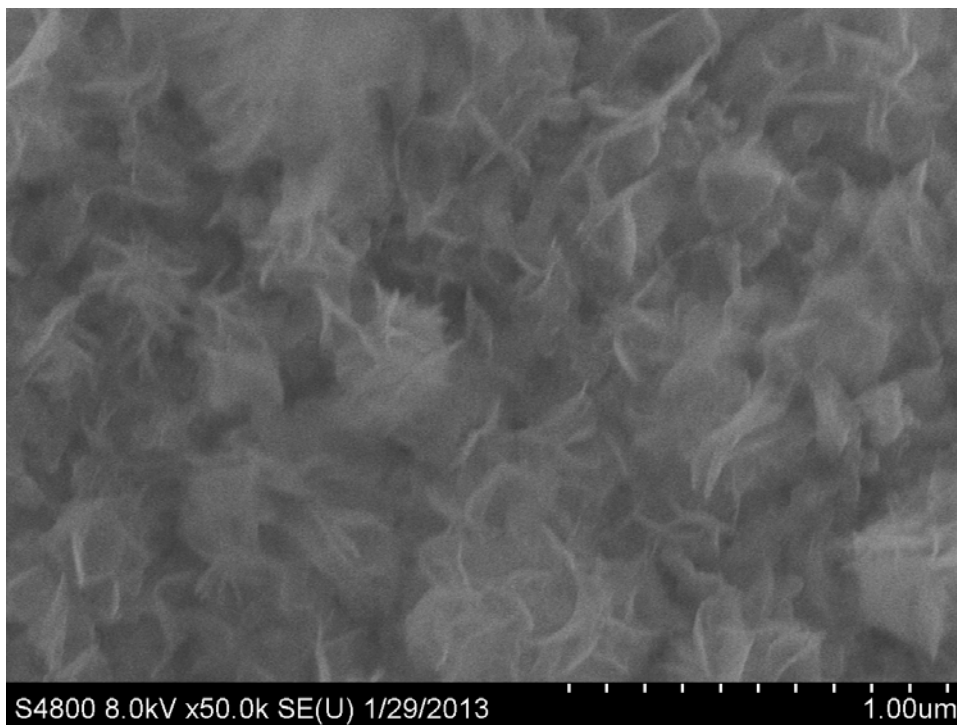
a) Full size SEM image of the cathode surface in 3000 mA h g<sub>carbon</sub><sup>-1</sup>.



b) Full size SEM image of the cathode surface in 5000 mA h g<sub>carbon</sub><sup>-1</sup>.

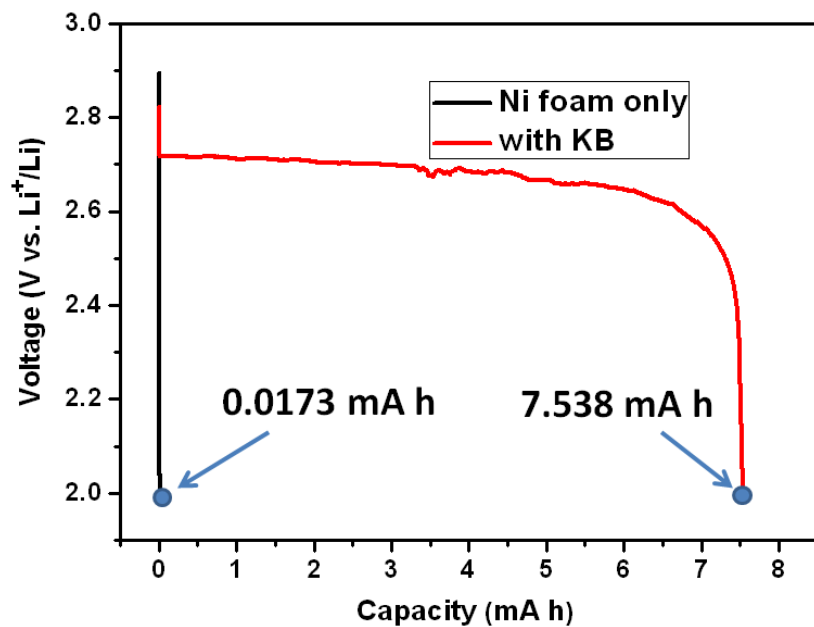


c) Full size SEM image of the cathode surface in 7000 mA h g<sub>carbon</sub><sup>-1</sup>.



d) Full size SEM image of the cathode surface in 9000 mA h g<sub>carbon</sub><sup>-1</sup>.

**Figure S4.** Discharge curves of Li-air batteries with bare nickel foam and air electrode in 1 M LiTFSI in TEGDME under  $0.25 \mu\text{A cm}^{-2}$  with a cut-off potential of 2.0 V vs.  $\text{Li/Li}^+$ . The contribution of current collector is negligible to total discharge capacity of the electrode.



**Figure S5.** XRD patterns of the discharged air-cathodes tested at the end of discharging progress. The strong peaks could be attributed to Ni and  $\text{Li}_2\text{O}_2$ , and the peaks of  $\text{LiCO}_3$ ,  $\text{LiOH}$ , or  $\text{Li-O-R}$  can't be observed.

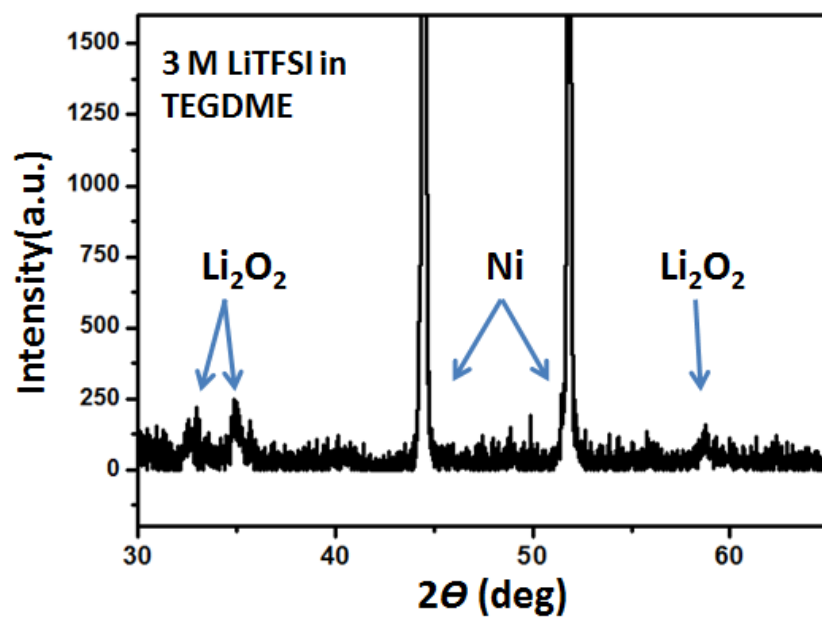


Figure S6. FTIR patterns of the discharge products in the 3M electrolyte.

