Electronic Supplementary Information (ESI)

All-Carbon-Nanofiber Electrodes for High-Energy Rechargeable Li-O_2 Batteries

Electrochemical Energy Laboratory, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139, USA. Tel: (617) 253-2259; E-mail: shaohorn@mit.edu

Materials for Micro and Nano Systems Group, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139, USA. Tel: (617) 253-1621; E-mail: cthomp@mit.edu

Index *Page*

Experimental details – Electrode fabrication

Fabrication of CNF electrodes. Commercially available porous anodized aluminum oxide (AAO) filters (Whatman, Anodisc 13) were used as porous supports for the growth of CNFs using atmospheric pressure chemical vapor deposition (AP-CVD). Thin films of Ta (30 nm)[1] and Fe (2 nm) were sequentially deposited onto one side of the filter under vacuum conditions (10^{-5} Torr), using electron beam evaporation. AP-CVD was performed in a custom growth system composed of a three-zone, 1-inch diameter tube furnace (Lindberg Blue) with gas flows regulated by a series of mass flow controllers (MKS, 1179A). After ramping to the growth temperature (700 °C) and annealing for 5 minutes in an H_2/Ar ambient, growth was initiated by introducing C_2H_4 into the AP-CVD system. CNF growth proceeded for 5-10 minutes before the system was purged with Ar and cooled to room temperature. The CNF carpet appeared as a visible black film (**Fig. S1a**) on the surface of the substrate after growth. HR-TEM (**Fig. S1b**) revealed a hollow nanofiber structure with an average diameter of 30 nm.

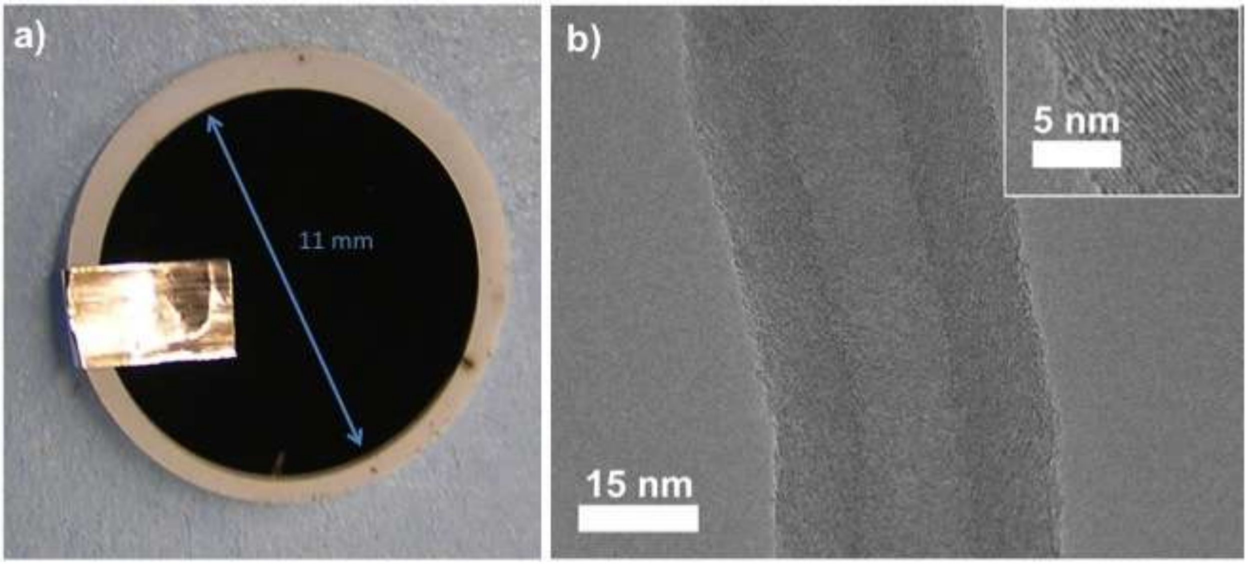

Fig. S1: Electrode Fabrication. a, Photograph of the filter after nanofiber synthesis. The filter diameter is 13 mm, and the area covered by CNFs has an 11 mm diameter. To prepare the electrode, a piece of aluminum foil is wrapped around one edge. b, High-resolution Transmission Electron Microscope (HR-TEM) bright field image of a typical nanofiber synthesized using this process. The average diameter of the fibers used in this study is roughly ~30 nm.

Experimental details – Mass measurement

Measurement of Carbon Mass. Mass measurements of the substrates were made using an ultra-microbalance (Mettler Toledo, XP6U) before and after the growth process. The CNF carpet mass was calculated as the difference between the two individual substrate mass measurements; the range of CNF masses used in this study was 44-184 μg. The experimental error on each mass measurement was determined to be ± 7 μg. The average mass loading of all samples was 0.11 ± 0.04 mg_C/cm^2_{geo}. Additionally, cyclic voltammetry was performed as a means to verify that the measured value is reasonable (**Fig. S2**).

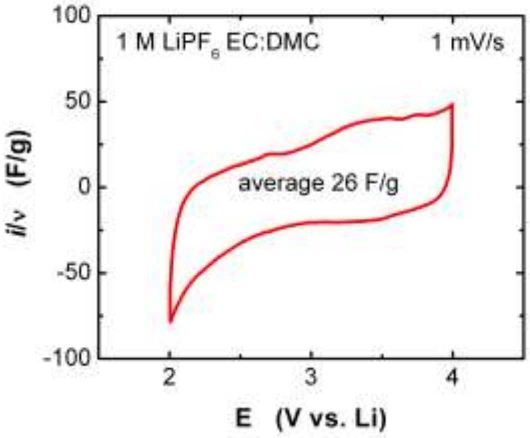

Fig. S2: Cyclic voltammetry of a CNF electrode in a Li cell (1 M $LiPF_6$ electrolyte in EC:DMC) indicated that CNF electrodes have an average capacitance of 26 F/g in the range 2.0 – 4.0 V vs. Li.

Experimental details – Cell assembly

Cell assembly and electrochemical measurements. CNF electrodes were prepared by attaching a small aluminum foil jumper around the edge of the as-synthesized electrode, to electronically connect the CNFs and Ta underlayer to the current collector, followed by drying in a vacuum oven at 60 °C (capacity evolution study) or 100 °C (high-rate and cycled samples) for 12 hours before use. Following drying, cells were assembled in an argon-filled glovebox (MBRAUN, USA, $H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm) in the following manner. A piece of lithium metal foil (15 mm in diameter and ~0.45 mm thick) served as the anode. Two Celgard 480 separators were pre-soaked in electrolyte (0.1 M $LiClO_4$ in 1,2-Dimethoxyethane (DME), battery grade, dry, 99.99% trace metals basis, Aldrich) and then placed on top of the lithium. An additional 140 µL of electrolyte was added before placement of the CNF electrode (CNF side facing towards separator). A stainless steel disk with holes drilled was used as the current collector for low-rate (<300 mA/g_C) tests while a piece of stainless steel mesh was used for all other tests. A schematic of an assembled cell is illustrated in **Fig. S3**. Following cell assembly, cells were removed from the glovebox, purged with DME-saturated O_2 for 5 minutes, and allowed to rest at open circuit for one hour. Li-O_2 cells were tested galvanostatically using a Solartron 1470 cell test unit in the voltage range 2.0 – 4.5 V vs. Li and at gravimetric currents ranging from 43 mA/g_C to 1000 mA/g_C. Geometric currents used in this study are fairly low compared to previous studies, owing to lower thicknesses (4-8 µm compared to 10-100 µm[2-4] or 200-800 µm[5, 6]) and lower densities of CNF electrodes.

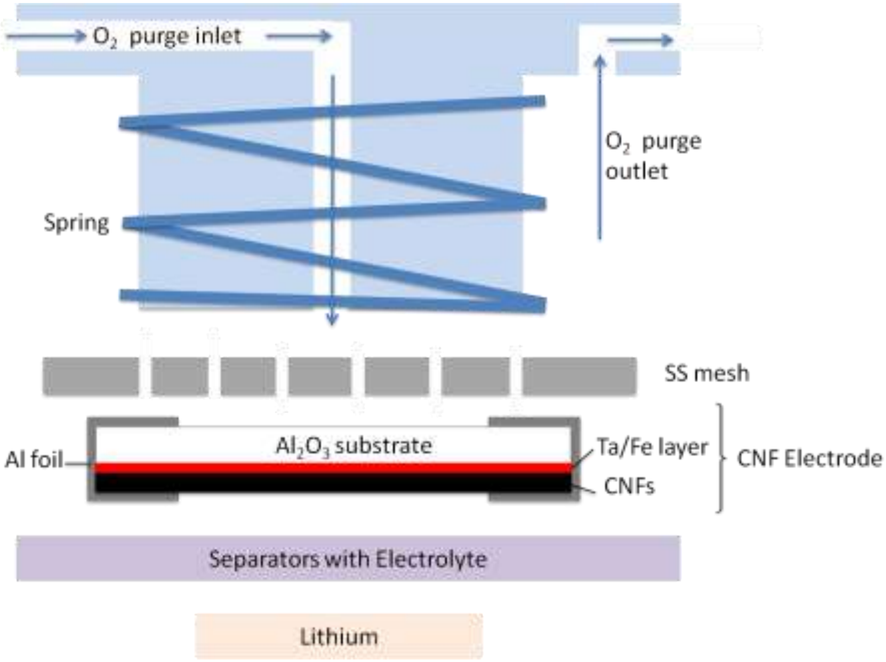

Fig. S3: CNF electrodes were tested in lithium cells with 0.1 M $LiClO_4$ electrolyte in DME and two porous Celgard C480 separators. The CNF electrode was placed with the carbon side facing towards the separator, and a porous stainless steel disk or mesh was used as both a current collector and a porous membrane to allow O_2 diffusion through to the porous AAO substrate. Following cell assembly in Argon, the cell was purged for 5 minutes with O_2 and sealed against the environment.

Experimental details – Physical characterization

X-Ray diffraction measurements. XRD scans of pristine and discharged CNF electrodes were collected using a Panalytical X'Pert Pro Multipurpose Diffractometer (Cu Kα). XRD samples were prepared inside the glovebox and sealed using Kapton film and vacuum grease to minimize exposure to air. A continuous scan rate of 0.12 °/min between 5 ° and 80 ° 2θ was used for pristine and discharged electrodes.

Scanning electron microscopy. Samples were prepared for cross-section SEM in an Ar-filled glovebox (MBRAUN, USA, $H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm) by first cleaving the porous AAO filters in half and then mounting them on standard SEM tilt-stubs using conductive carbon tape. High-resolution images were captured at 5 kV accelerating voltage at a ~5 mm working distance using a JEOL 6320FV field-emission high-resolution SEM.

Transmission electron microscopy. Samples were prepared for TEM by scraping the CNF carpet onto a Holey carbon TEM grid using a clean razor blade. Bright field images were captured at 200 keV using a JEOL 2010 TEM.

Experiment reproducibility

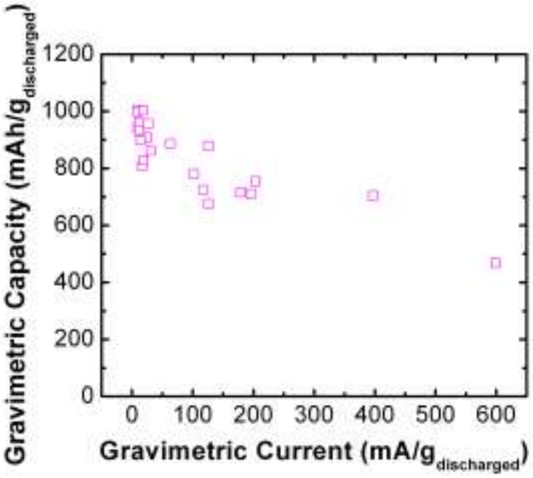

Fig. S4: Reproducibility of discharge capacity normalized to the weight of discharged electrodes (C + Li_2O_2) of CNF electrodes in O_2 cells tested over a range of gravimetric electrode currents (lower cutoff of 2.0 V vs. Li).

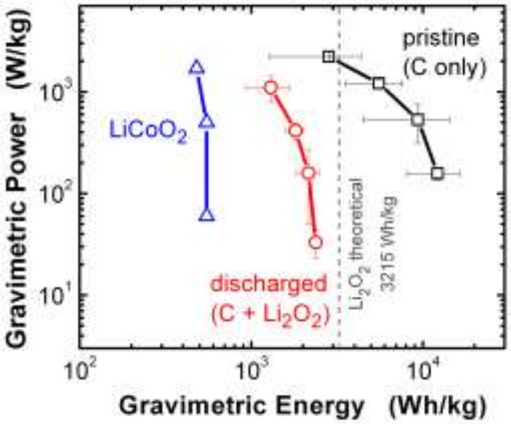

Fig. S5: Ragone plot representing the average performance over all samples (data points in **Fig. S4**). Four data points for each curve in the Ragone plot were obtained by averaging the gravimetric energy and power for samples tested in the range <70 mA/g_C (9 samples), 70 – 300 mA/g_C (8 samples), 300 – 600 mA/g_C (4 samples), or >600 mA/g_C (2 samples). Error bars represent the standard deviation of gravimetric energies and powers in each current range. Gravimetric energy and power of $LiCoO_2$ electrodes are shown for comparison.[7]

Gravimetric capacity calculation

Gravimetric capacities were calculated by normalizing the measured charge from galvanostatic testing, q_{measured}, by either the mass of carbon, m_{C}, or the mass of the discharged electrode, $m_{\text{C}} + m_{\text{Li2O2}}$.

$$q_{\text{C-only}} = \frac{q_{\text{measured}}}{m_{\text{C}}} \ \left[\text{mAh/g}_{\text{C}}\right]$$

$$q_{\text{discharged}} = q_{\text{C+Li}_2\text{O}_2} = \frac{q_{\text{measured}}}{m_{\text{C}} + q_{\text{measured}} / \rho^*_{\text{Li}_2\text{O}_2}} \ \left[\text{mAh/g}_{\text{C+Li}_2\text{O}_2}\right]$$

$$\rho^*_{\text{Li}_2\text{O}_2} = 1169 \left[\text{mAh/g}_{\text{Li}_2\text{O}_2}\right]$$
$$q_{\text{measured}} \equiv \left[\text{mAh}\right]$$
$$m_{\text{C}} \equiv \left[\text{g}\right]$$

The average CNF carpet mass used in this study was found to be 105 μg$_{\text{C}}$ (0.11 ± 0.04 mg$_{\text{C}}$/cm$^2_{\text{geo}}$), whereas the average mass of Li_2O_2 discharge product, corresponding to the average low rate (<70 mAh/g$_{\text{C}}$) discharge capacity (4720 mAh/g$_{\text{C}}$), was found to be 434 μg$_{\text{Li2O2}}$, ~4 times heavier than the carbon mass.

Theoretical energy density calculation

The theoretical energy density of Li_2O_2 can be calculated by using Faraday's law to first determine the theoretical capacity for Li_2O_2:

$$\rho^*_{\text{Li2O2}} = \frac{F \times Z_r}{M} = 1169 \ \text{Ah/kg}_{\text{Li}_2\text{O}_2}$$

$$F = 96500 \ \text{C/mol} \ = 26.81 \ \text{Ah/mol}$$
$$Z_r = 2 \ \text{electrons, unitless}$$
$$M = 45.88 \times 10^{-3} \ \text{kg}_{\text{Li}_2\text{O}_2}\text{/mol}$$

The theoretical energy density can then be calculated by multiplying the theoretical capacity by the average practical discharge voltage for Li-O_2 cells (2.75 V vs. Li)[8]:

$$1169 \ \text{Ah/kg}_{\text{Li}_2\text{O}_2} \times 2.75 \ \text{V vs. Li} = 3215 \ \text{Wh/kg}_{\text{Li}_2\text{O}_2}$$

Likewise, the theoretical energy density of Li_2O can be calculated using the above calculations but instead using a molar mass, M, of 29.88 × 10^{-3} kg$_{\text{Li2O}}$/mol. The resulting energy density for Li_2O is

$$\rho^*_{\text{Li}_2\text{O}} \times V_{\text{discharged}} = 1795 \ \text{Ah/kg}_{\text{Li}_2\text{O}} \times 2.75 \ \text{V vs. Li} = 4935 \ \text{Wh/kg}_{\text{Li}_2\text{O}}$$

Li_2O_2 toroid images

Low-rate discharge morphology.

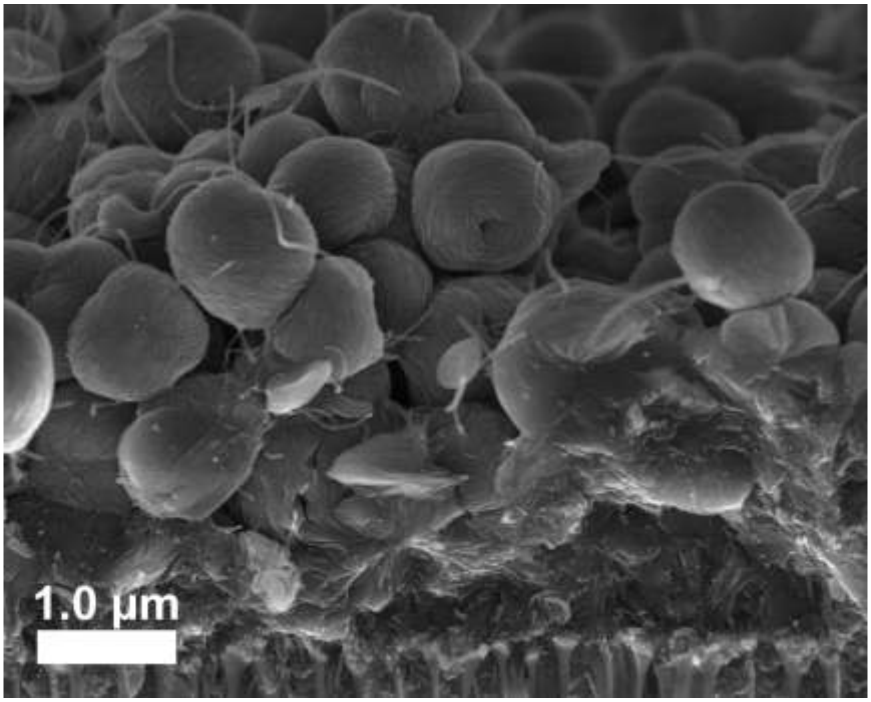

Fig. S6: SEM image of discharged electrode (46 mA/g_C). Image corresponds to a gravimetric capacity of 4240 mAh/g_C obtained with a lower voltage cutoff of 2.0 V vs. Li.

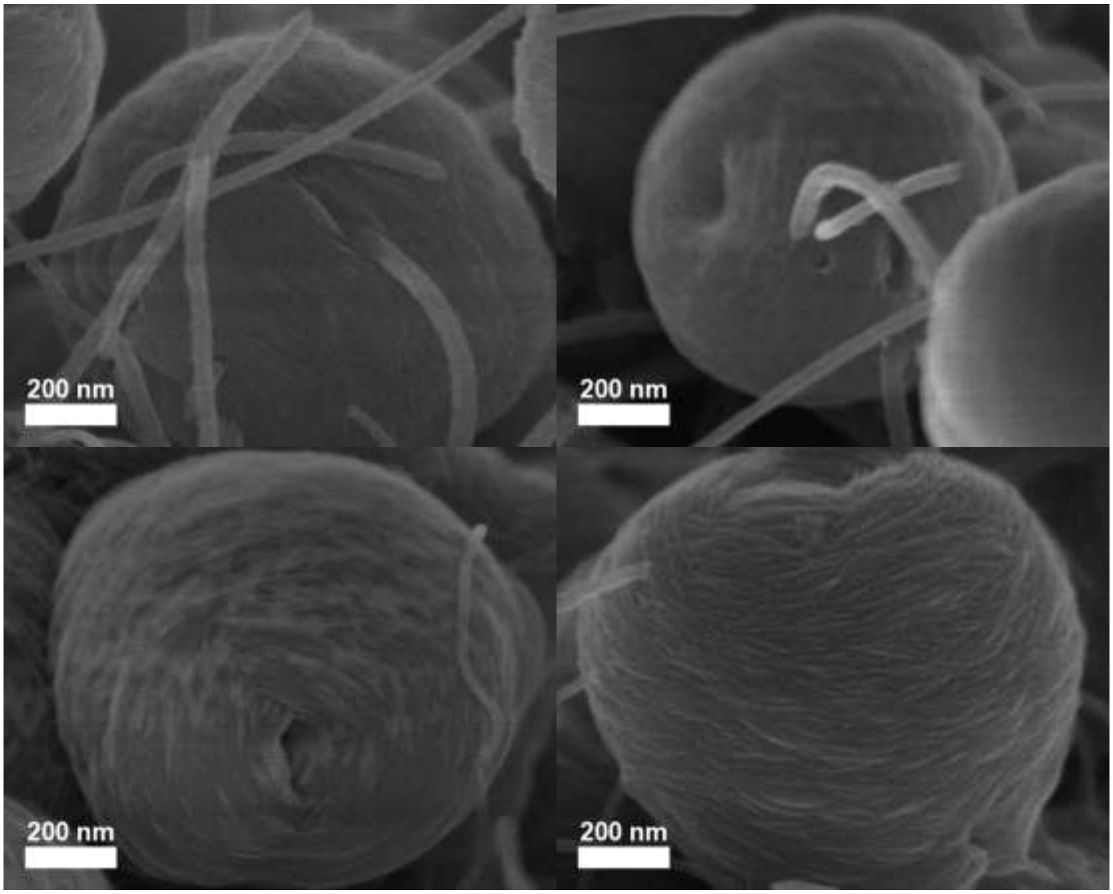

Fig. S7: SEM image of discharged electrode (46 mA/g_C). Image corresponds to a gravimetric capacity of 4240 mAh/g_C obtained with a lower voltage cutoff of 2.0 V vs. Li.

High-rate discharge morphology.

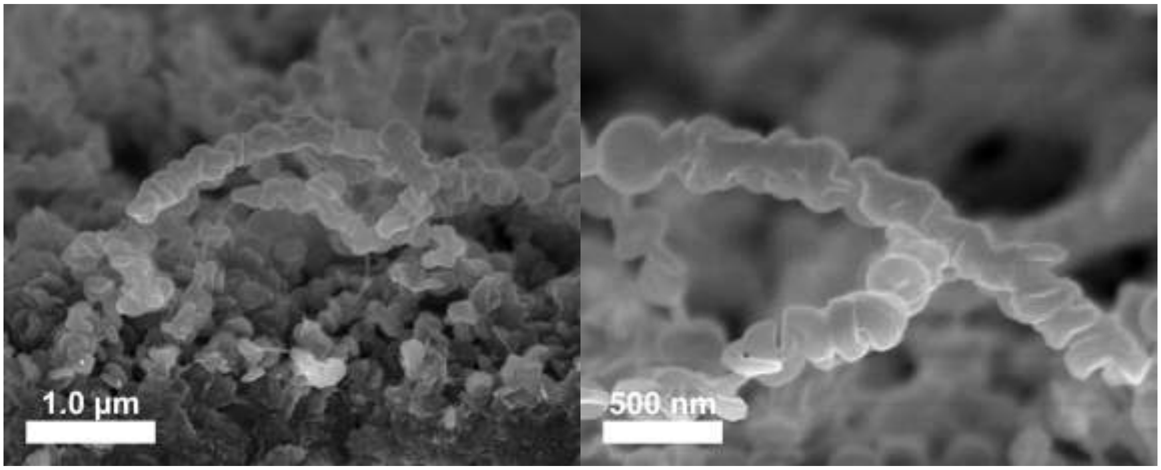

Fig. S8: **SEM of Discharged Electrode (511 mA/g_C).** Cross-sectional SEM of an electrode discharged at 511 mA/g_C with a lower voltage cutoff of 2.0 V vs. Li. The image corresponds to a gravimetric discharge capacity of 3560 mAh/g_C (879 mAh/$g_{discharged}$). The electrode morphology is characterized by a dense discharge product near the AAO surface, but a very low-density morphology near the top of the carpet. CNFs are conformally coated with comparatively smaller particles than particles observed at low discharge rates (46 mA/g_C).

References

1. G. D. Nessim, M. Seita, K. P. O'Brien, A. J. Hart, R. K. Bonaparte, R. R. Mitchell and C. V. Thompson, *Nano Lett.*, 2009, **9**, 3398-3405.
2. G. Q. Zhang, J. P. Zheng, R. Liang, C. Zhang, B. Wang, M. Hendrickson and E. J. Plichta, *J. Electrochem. Soc.*, 2010, **157**, A953-A956.
3. Y. C. Lu, Z. C. Xu, H. A. Gasteiger, S. Chen, K. Hamad-Schifferli and Y. Shao-Horn, *J. Am. Chem. Soc.*, 2010, **132**, 12170-12171.
4. K. M. Abraham and Z. Jiang, *J. Electrochem. Soc.*, 1996, **143**, 1-5.
5. J. Read, *J. Electrochem. Soc.*, 2002, **149**, A1190-A1195.
6. S. S. Zhang, D. Foster and J. Read, *J. Power Sources*, 2010, **195**, 1235-1240.
7. H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J.-M. Tarascon, *ChemSusChem*, 2008, **1**, 348-355.
8. Y. C. Lu, H. A. Gasteiger, M. C. Parent, V. Chiloyan and Y. Shao-Horn, *Electrochem. Solid-State Lett.*, 2010, **13**, A69-A72.