

Cite this: DOI: 10.1039/c0xx00000x

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Achieving electrochemical capacitor functionality from a traditional battery material: conformal, nanoscale LiMn_2O_4 coatings on 3-D, device-ready carbon nanoarchitectures

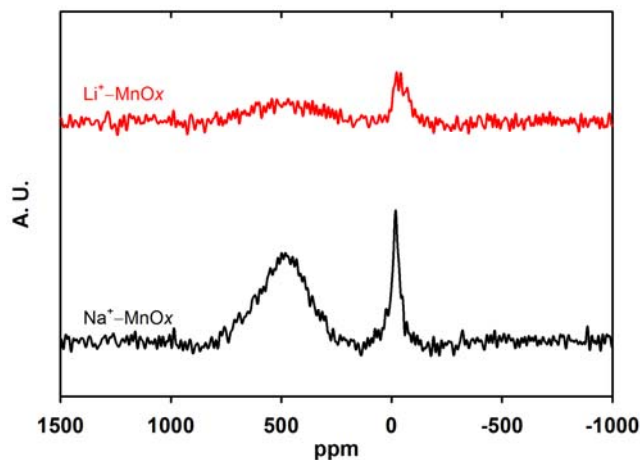
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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

XAS experimental details

10 The K-edge absorption was isolated by fitting the pre-edge region (6239–6439 eV) with a quadratic polynomial, extrapolating over the entire range of the spectrum, and subtracting the pre-edge background from the entire spectrum. Step normalization was applied using the atomic absorption,
15 which was determined by fitting the post edge region (6639–8040 eV) with a cubic polynomial. The photoelectron wave number was derived by setting the inner potential to the inflection point energy. The extended X-ray absorption fine structure (EXAFS) data, $\chi(k)$, were extracted using multi-node
20 cubic spline procedures applied to k^3 -weighted spectra over the k -range of 2.0–15.0 \AA^{-1} . The post-edge background was optimized by minimizing the amplitude of non-physical peaks in the 0–0.9 \AA region of the Fourier transform. The data analysis
25 up to this point was carried out using the WinXAS software package (version 3.1).^{1,2} The Fourier transforms presented here were generated with k^3 -weighted EXAFS spectra over the range 3.0–15 \AA^{-1} and a Hanning window of 1.0 \AA^{-1} using the curve fitting code FEFFIT (version 2.984) of the University of
Washington XAFS (UWXAFS) software package.³



30 **Fig. S1.** Solid-state ^{23}Na nuclear magnetic resonance spectra of $\text{Na}^+\text{-MnO}_x$ (—) and $\text{Li}^+\text{-MnO}_x$ (—).

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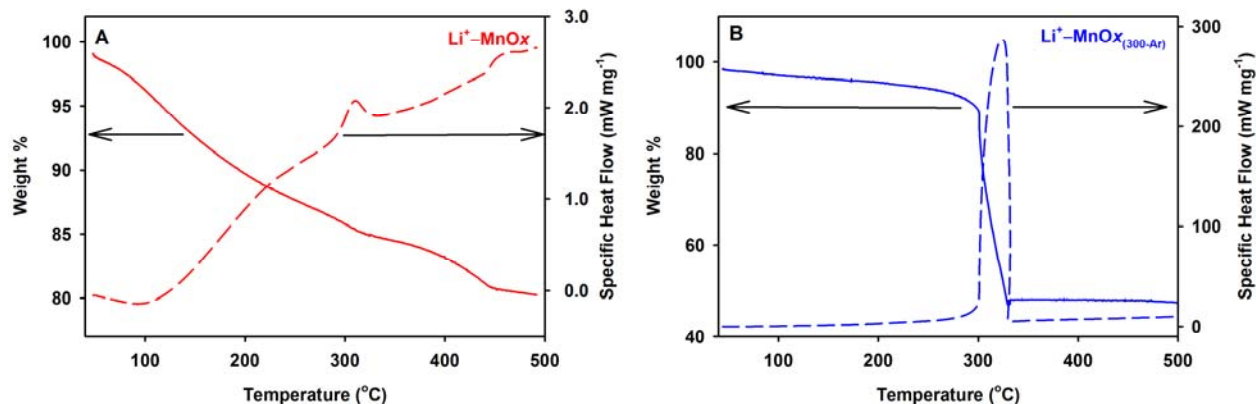


Fig. S2. Thermal gravimetric analysis (—) and differential scanning calorimetry (---) of (A) $\text{Li}^+\text{-MnO}_x$ in an argon atmosphere and (B) $\text{Li}^+\text{-MnO}_x(300\text{-Ar})$ in an oxygen atmosphere.

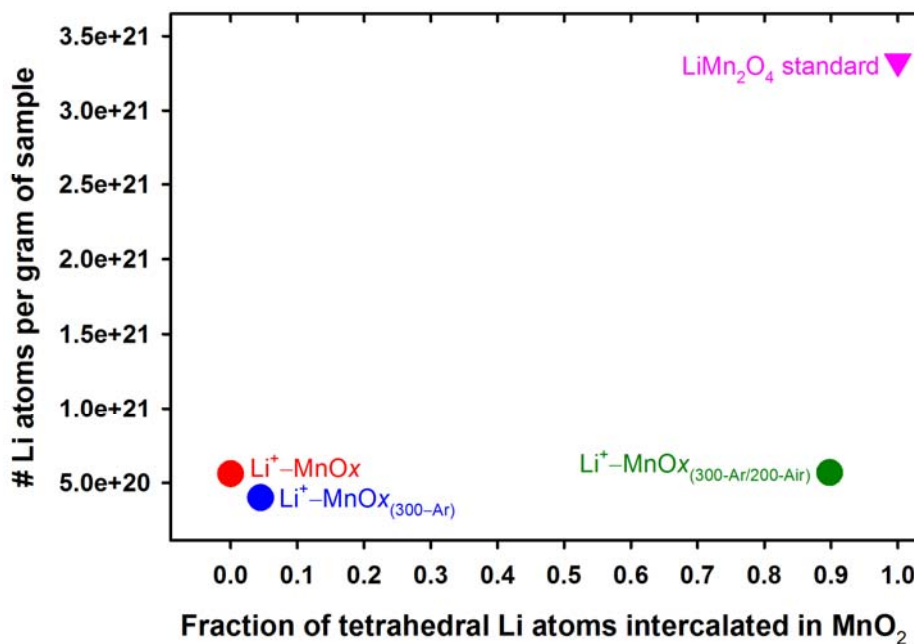


Fig. S3. Plot of # of Li atoms per gram of sample versus fraction of Li atoms in tetrahedral site derived from solid-state ^7Li NMR for LiMn_2O_4 standard (\blacktriangledown), $\text{Li}^+\text{-MnO}_x$ (\bullet), $\text{Li}^+\text{-MnO}_x(300\text{-Ar})$ (\bullet), and $\text{Li}^+\text{-MnO}_x(300\text{-Ar}/200\text{-Air})$ (\bullet).

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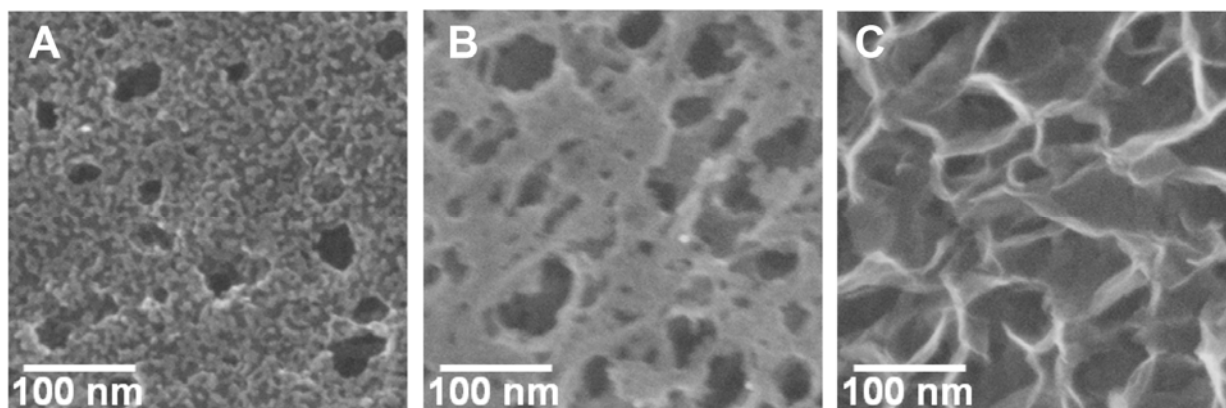


Fig. S4. Scanning electron micrographs of the exterior surface of (A) $\text{Li}^+\text{-MnO}_x(300\text{-Ar}/200\text{-Air})$, (B) $\text{Li}^+\text{-MnO}_x(300\text{-Ar}/200\text{-Air})$ after 200 voltammetric cycles in 2.5 M Li_2SO_4 , and (C) $\text{Li}^+\text{-MnO}_x(300\text{-Ar}/200\text{-Air})$ after 200 cycles in 2.5 M $\text{Li}_2\text{SO}_4 + 20$ mM NaHCO_3 .

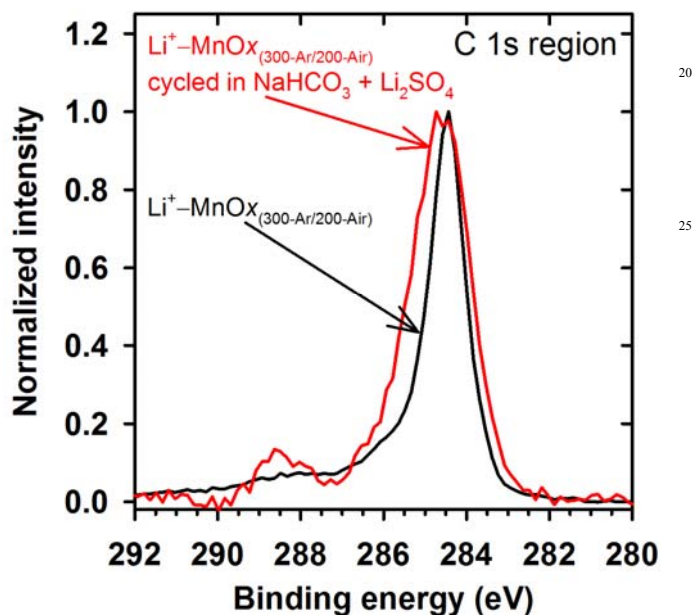


Fig. S5. X-ray photoelectron C 1s spectra of $\text{Li}^+\text{-MnO}_x(300\text{-Ar}/200\text{-Air})$ (—) and $\text{Li}^+\text{-MnO}_x(300\text{-Ar}/200\text{-Air})$ after 200 voltammetric cycles in 2.5 M $\text{Li}_2\text{SO}_4 + 20$ mM NaHCO_3 (—).

Notes and references

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S1. T. Ressler, *J. Synchrotron Radiat.*, 2000, **5**, 118.

S2. T. Ressler, *J. Phys. IV*, 1997, **7**, C2-269.

S3. E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, and D. Haskel, *Physica B*, 1995, **208-209**, 117.