Supporting Information

Electrochemical behavior and surface structural change of $LiMn_2O_4$ charged to 5.1 V

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SECTION S1:

Important notes on XPS fitting: Multiplet splitting and shakeup features within the Mn 2p spectra act to complicate the analysis of XPS data. Multiplet splitting can be described in simple terms as an energy coupling interaction between unpaired electrons in the valence shell and unpaired electrons within the core level which occurs following the excitation of core level electrons during the photoemission process.[1, 2] The result of this energy coupling for manganese is that Mn 2p spectra taken from a single chemical species contain several multiplet peaks over an broad energy range (~10eV). Another spectral feature known to affect the analysis of Mn 2p spectra are shakeup features that arise from photoelectrons that have lost energy through the promotion of valence electrons from an occupied energy to a higher unoccupied level. While these factors greatly complicate the analysis, Nesbit et al.[1] have outlined curve fitting parameters that can be used for the deconvolution of Mn 2p photoemission spectra taken from a number of specific Mn-based chemical species. In this study these curve fitting parameters were used to curve fit $Mn2p_{3/2}$ spectra taken from $LiMn_2O_4$ of charged states. The XPS core level spectra were curve fitted using Voigt profiles composed of 70% Gaussian and 30% Lorentzian line shapes and using a Shirley-type background. The full width at half-maximum of all the curve fitted peak was 1eV, with permission of slightly adjustment. The fitting results are similar to the previous works (Table S4), the FWHM depends on the instrument used,[3] and shorter FWHM indicates better resolution of the instrument.

Table S1 Mn($2p_{3/2}$) peak parameters for Mn in the pristine state

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{2+}(total)= 2.4			
Mn^{2+}	640.3	1	1.83
Mn^{2+}	641.4	1	0.46
Mn^{2+}	642.2	1	0.05
Mn^{2+}	643.1	1	0.05
Mn^{2+}	644.2	1	0.03
Mn^{3+}(total)=48.9			
Mn^{3+}	641.1	1	13.76
Mn^{3+}	641.8	1	13.76
Mn^{3+}	642.8	1	19.29
Mn^{3+}	643.7	1	1.15
Mn^{3+}	645.1	1	0.92
Mn^{4+}(total)=48.7			
Mn^{4+}	642.3	1	14.97
Mn^{4+}	643.4	1	16.05
Mn^{4+}	644.3	1	12.49
Mn^{4+}	645.3	1	3.59
Mn^{4+}	646.2	1	1.61

Table S2 Mn($2p_{3/2}$) peak parameters for Mn in the charged state (5.1 V)

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{2+}(total)= 9.3			
Mn^{2+}	640.1	1	3.08
Mn^{2+}	641.3	1	2.67
Mn^{2+}	642.1	1	1.54
Mn^{2+}	643.0	1	1.23
Mn^{2+}	644.4	1	0.82
Mn^{3+}(total)=27.4			
Mn^{3+}	640.9	1	6.97
Mn^{3+}	641.7	1	6.97
Mn^{3+}	642.3	1	9.24
Mn^{3+}	643.5	1	2.87
Mn^{3+}	644.9	1	1.38
Mn^{4+}(total)=63.2			
Mn^{4+}	642.3	0.97	25.72
Mn^{4+}	643.3	0.98	21.53
Mn^{4+}	644.2	1	8.89
Mn^{4+}	645.2	1	4.44
Mn^{4+}	646.2	1	2.66

Table S3 Mn($2p_{3/2}$) peak parameters for Mn in the discharged state (3 V)

Peak	B.E. (eV)	FWHM (eV)	Percent (%)
Mn^{2+}(total)= 4.2			
Mn^{2+}	640.2	1	1.52
Mn^{2+}	641.1	1	1.19
Mn^{2+}	642.1	1	1.05
Mn^{2+}	643.0	1	0.33
Mn^{2+}	644.2	1	0.07
Mn^{3+}(total)=47.5			
Mn^{3+}	641.1	1	12.55
Mn^{3+}	641.8	1	12.55
Mn^{3+}	642.8	1	16.82
Mn^{3+}	643.8	1	3.77
Mn^{3+}	645.2	1	1.83
Mn^{4+}(total)=48.3			
Mn^{4+}	642.5	1	13.91
Mn^{4+}	643.5	1	15.45
Mn^{4+}	644.3	1	11.80
Mn^{4+}	645.3	1	4.66
Mn^{4+}	646.4	1	2.50

Table S4 Mn($2p_{3/2}$) peak parameters in the literature for comparison[4]

Peak	B.E. (eV)	FWHM (eV)
Mn(II) MnO		
Mn^{2+}	640.2	1.21
Mn^{2+}	641.1	1.21
Mn^{2+}	642.1	1.21
Mn^{2+}	643.0	1.21
Mn^{2+}	644.2	1.21
Mn(III) Manganite (MnOOH)		
Mn^{3+}	641.2	1.25
Mn^{3+}	641.9	1.25
Mn^{3+}	642.7	1.25
Mn^{3+}	643.7	1.25
Mn^{3+}	645.1	1.25
Mn(IV), Birnessite (MnO_2)		
Mn^{4+}	642.5	1.25
Mn^{4+}	643.5	1.3
Mn^{4+}	644.3	1.3
Mn^{4+}	645.3	1.3
Mn^{4+}	646.4	1.25

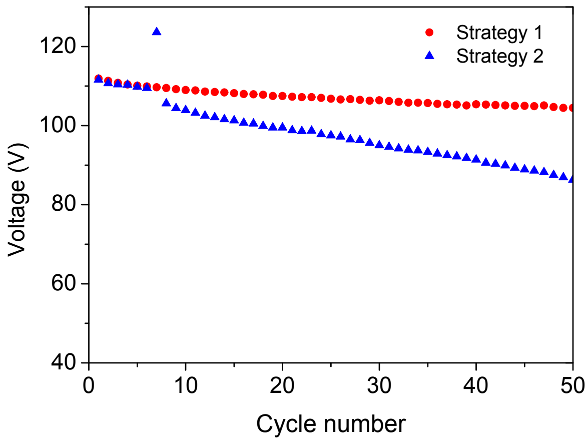

Fig.S1 Cycling performance of the two strategies

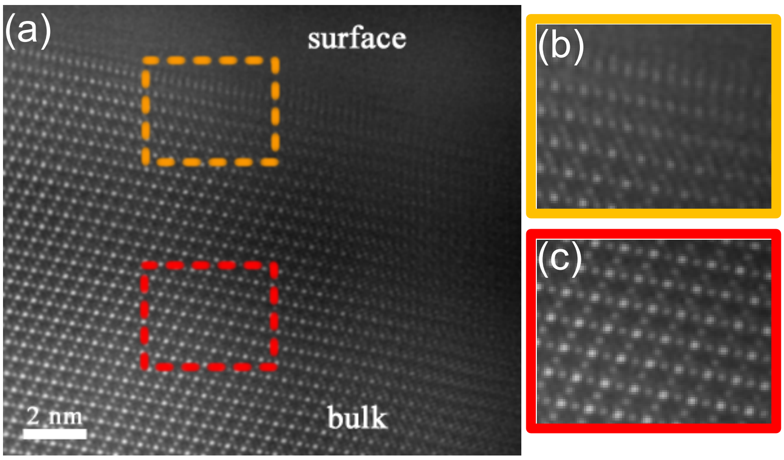

Fig.S2 (a) HAADF image taken along the [110] zone axes of another $LiMn_2O_4$ particle charged to 5.1 V; (b)(c) magnified regions as indicated by orange dashed square and red dashed square respectively

References

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2. Casey, P.; McCoy, A. P.; Bogan, J.; Byrne, C.; Walsh, L.; O'Connor, R.; Hughes, G. *Journal of Physical Chemistry C* **2013,** 117, (31), 16136-16143.
3. Biesinger, M. C.; Payne, B. P.; Hart, B. R.; Grosvenor, A. P.; McIntryre, N. S.; Lau, L. W. M.; Smart, R. S. C. *Proceedings of the 17th International Vacuum Congress/13th International Conference on Surface Science/International Conference on Nanoscience and Technology* **2008,** 100.
4. Biesinger, M. C.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. *Applied Surface Science* **2010,** 257, (3), 887-898.