Exploiting Na$_2$MnPO$_4$F as a high-capacity and well-reversible cathode material for Na-ion batteries

Xiaochen Lin, Xu Hou, Xiaobiao Wu, Sihui Wang, Ming Gao, Yong Yang*

State Key Laboratory of Physical Chemistry of Solid Surfaces, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China. E-mail: yyang@xmu.edu.cn

1. The *ex-situ* XPS measurements

Mn 3s level is known to exhibit multiplet splitting (ΔE_{3s}), which is an indicator for the Mn valence[1-4]. Therefore, we utilize the *ex-situ* XPS measurements of Mn 3s to prove the existence of Mn^{2+} and study the variation trend of Mn valence during cycling.

The *ex-situ* XPS spectra and multiplet splitting in differernt charge/discharge states are shown in Fig. S1 and Table. S1.
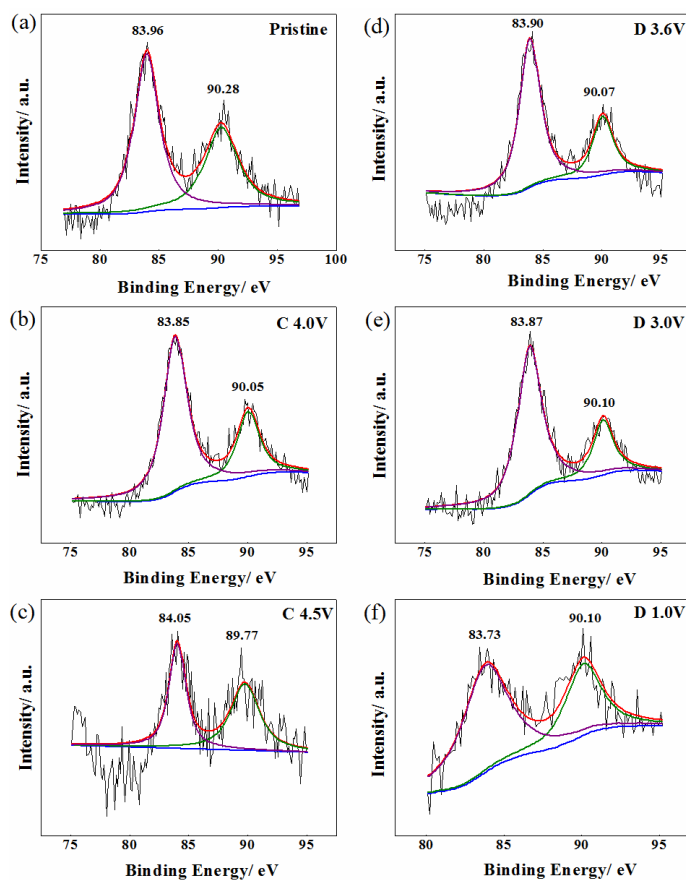

Fig. S1 *Ex-situ* XPS spectra of differernt charge/discharge states: (a) pristine; (b) charge to 4.0 V; (c) charge to 4.5 V; (d) discharge to 3.6 V; (e) discharge to 3.0 V; (f) discharge to 1.0 V.

Table. S1 The multiplet splitting of Mn 3s at differernt charge/discharge states in XPS

States	ΔE_{3s} /eV
Pristine	6.32
C 4.0V	6.10
C 4.5V	5.72
D 3.6V	6.17
D 3.0V	6.23
D 1.0V	6.37

The ΔE_{3s} of pristine sample is 6.32 eV, which is between the reported ΔE_{3s} values of Mn^{2+} in sulphides (6.2 eV)[4] and spinel material (6.5 eV)[1-3]. Owing to few reports about XPS of Mn 3s in polyanionic cathode material, we can roughly confirm the existence of divalent Mn in Na_2MnPO_4F material.

The *ex-situ* XPS results also show that ΔE_{3s} decrease from 6.32 eV to 5.72 eV when charged to 4.5V, corresponding to the change of Mn valence from Mn^{2+} to Mn^{3+}. Then in the discharge process, the trend is opposite as the Mn valence turns back to Mn^{2+}. Therefore, the changes of Mn valance during cycling can be qualitatively studied through *ex-situ* XPS.

2. The calculation of Na^+ diffusion coefficient

The below formula we used to calculate Na^+ diffusion coefficient is one simplified formula. It applies to planar diffusion in a slab of homogeneous material with a linear dependency of E-$t^{1/2}$ and good equilibration during the relaxation period. According to equation (1) derived from Sand equation[5], we can calculate the apparent chemical diffusion coefficient value.
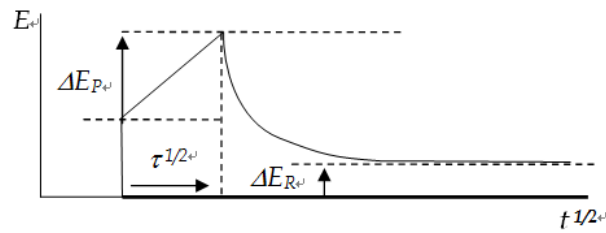
$$\frac{dE}{dt^{1/2}} = \frac{2j}{C_V (\pi D)^{1/2}} \tag{1}$$

$$\frac{\Delta E_P}{\tau^{1/2}} = \frac{2I}{AC_V (\pi D)^{1/2}} \qquad \Delta E_P = \frac{2I\tau^{1/2}}{AC_V (\pi D)^{1/2}}$$

$$\Delta E_R = \frac{\Delta Q}{C} = \frac{\Delta Q}{VC_V} = \frac{I\tau}{VC_v}$$

$$\frac{\Delta E_R}{\Delta E_P} = \frac{\tau^{1/2}(\pi D)^{1/2} A}{2V} = \frac{\tau^{1/2}(\pi D)^{1/2}}{2L}$$

$$D = \left(\frac{4}{\pi}\right)\left(\frac{L^2}{\tau_P}\right)\left(\frac{\Delta E_{RELAX}}{\Delta E_{PULSE}}\right)^2$$

Where L is the ratio of active material volume to the surface area perpendicular to the current ($L=10^{-5}$ cm observed from the SEM images), and τ_P is the pulse duration ($\tau_P=1800$ s). Combined the ΔE_{PULSE} values obtained from E-t$^{1/2}$ plots with the ΔE_{RELAX} values obtained from E-t plots, we could calculate the simplified Na$^+$ diffusion coefficient.

References

1   D. A. Shirley, *Phys. Scr.*, 1975, **11**, 117.
2   V. A. M. Brabers, F. M. van Setten and P. S. A. Knapen, *J. Solid State Chem.*, 1983, **49**, 93-98.
3   G. C. Allen, S. J. Harris, J. A. Jutson and J. M. Dyke, *Appl. Surf. Sci.*, 1989, **37**, 111-134.
4   V. Tsurkan, M. Demeter, B. Schneider, D. Hartmann and M. Neumann, *Solid State Commun.*, 2000, **114**, 149-154.
5   A. J. Bard and L. R. Faulkener, *Electrochemical Methods*, 2nd Edition edn., 2001.