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Exploring Reversible Oxidation of Oxygen in a Manganese Oxide

Ke Du[1,2], Jinyou Zhu[1], Guorong Hu, Hongcai Gao[2], Yutao Li[2], and John B. Goodenough[2]*

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Nominal $Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ with the layered P3 structure (s.g. R3m) showed XPS evidence of holes in the O-*2p* bands on removal of Na^+ ions. A large voltage plateau at 4.1 V versus Na^+/Na faded significantly over 50 cycles although the capacity in the range $20 \le V < 4.5$ V remained unchanged. Oxidation of the O-*2p* bands is not reversible.

Keywords: Oxygen oxidation, manganese oxides, redox-energy pinning

Introduction

Reversible oxidations of the O-*2p* band in oxides containing cationic *4d* and *5d* energies near the top of the O-*2p* bands have been reported [1-4], and it is explained by M (d) – O (p) hybridization [5]. A question arises whether this phenomenon can be observed with oxides containing cationic *3d* states near the top of the O-*2p* bands [6-10]. Whether reversible oxidation of the oxide ions of a transition-metal oxide can be distinguished from oxidation of a d-state redox couple pinned at the top of the O-*2p* bands remains an open question, and Mn(IV) oxides provide an opportunity to explore this question with a *3d* redox couple since the Mn(V)/Mn(IV) redox couple lies far enough below the top of the O-*2p* bands that octahedral-site Mn(V) states in oxides are not found; the reaction 2Mn(V) = Mn(IV) + Mn(VI) with tetrahedral-site Mn(VI) is more stable than Mn(V). We find that electrochemical removal of Na^+ from layered $Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ gives a flat voltage plateau near 4.2 V versus Na^+/Na with the introduction of holes into the O-*2p* bands of the bulk oxide, but a capacity fade of the voltage plateau on cycling suggests oxidation of the O-*2p* bands is not reversible in this oxide with the possibility that an amorphous second phase is formed.

Experimental

LiOH (98%, Aldrich), Na_2CO_3 (99.99%, Aldrich), and MnO_2 (99.8%) were used as received; they were thoroughly mixed and calcined at 700°C for 24 h to obtain the final product. The heating and cooling rates of the powders were, respectively, 4°C and 2°C min^{-1}.

Electrochemical tests were made with CR2032 coin cells containing a metallic-Na anode, a glass-fiber separator, a liquid electrolyte of 1 M $NaClO_4$ in a 9:1 mixture of propylene carbonate (PC) and fluorethylene carbonate (FEC), and a cathode of 80% active material with 10 w% carbon and 10 w% PVDF binder. Cells were cycled galvanostatically with an MTI battery testing system at room temperature.

For XPS and *ex situ* XRD, the cells were disassembled at different states of charge and the cathodes were washed three times in dimethyl carbonate (DMC) before drying, all in a glove box. The samples were taped to a glass substrate for measurement outside the glove box.

Results

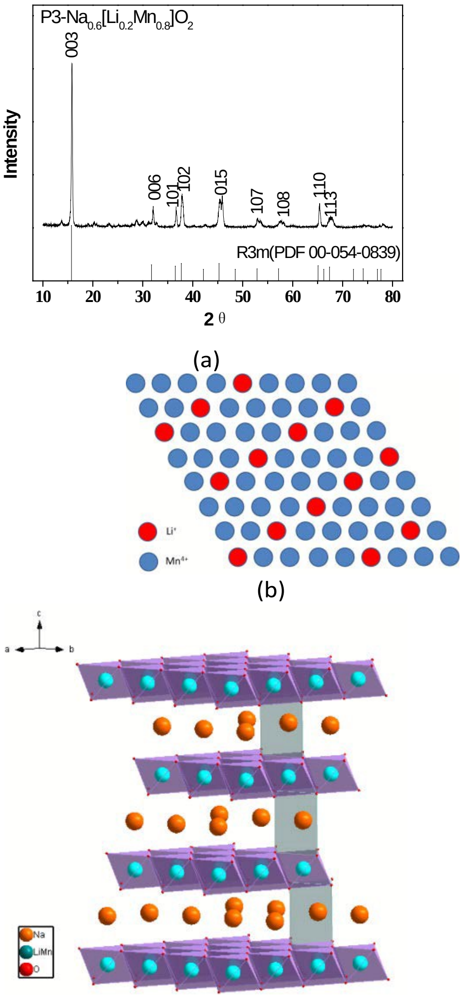
The main peaks of the XRD pattern of nominal $Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ shown in Fig. 1(a) fit well those of a layered *P3* oxide with space group *R3m* in which the Na^+ ions occupy trigonal prismatic sites between close-packed layers of octahedral-site $(Li_2Mn_{0.8})O_{6/3}$ sharing common edges. The P3 and P2 structures have, respectively, cubic and hexagonal layer stacking with Na in trigonal-prismatic sites, the O3 structure has cubic stacking with Na in octahedral sites. Some minor peaks between 20° and 32° 2θ were not identified. should be caused by ordered arrangement of Li/Mn in transition metal layer (Fig.1b). The XRD peaks besides (00l) are broadened, meaning stacking faults may be happened in this *P3* structured sample (Fig.1c) [10], which makes the Rietveld refine impossible.

[1.] School of Metallurgy and Enviroment, Central South University, Changsha 410083, China.
[2.] Texas Materials Institute and Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX, USA.

* Corresponding author E-mail: jgoodenough@mail.utexas.edu

Fax: 512-471-7612

Tel: 512-471-1646



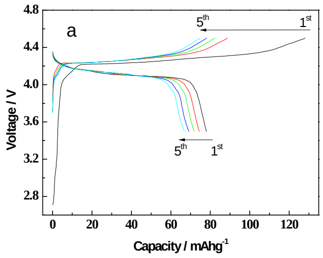
(a)

(b)

(c)

Figure 1 Structure of $Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ (a. XRD pattern; b. ordered Li/Mn atoms cc) the P3 structure.

The charge/discharge curves of a cell cycled between 3.5 and 4.5 V versus sodium at a rate of 10 mA g^{-1} show, in Fig. 2(a), a long plateau at $V \approx 4.2$ V, which is associated with the oxidation of the O-$2p^6$ band. Since the initial solid-electrolyte interphase (SEI) passivating layer of the anode contains Na^+ from the cathode, the continuing capacity fade with cycling would appear to signal an irreversible loss of alkali ions from the cathode. On cycling from 2.0 to 4.5 V at 15 mA g^{-1}, Fig. 2(b), the total discharge capacity initially increases slightly before decreasing; but the length of the long plateau at 4.1 V on discharge decreases progressively with cycling as in Fig. 2(a).



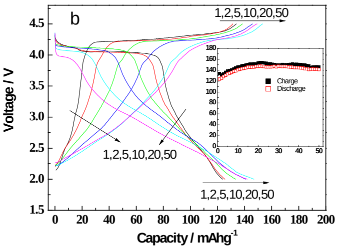
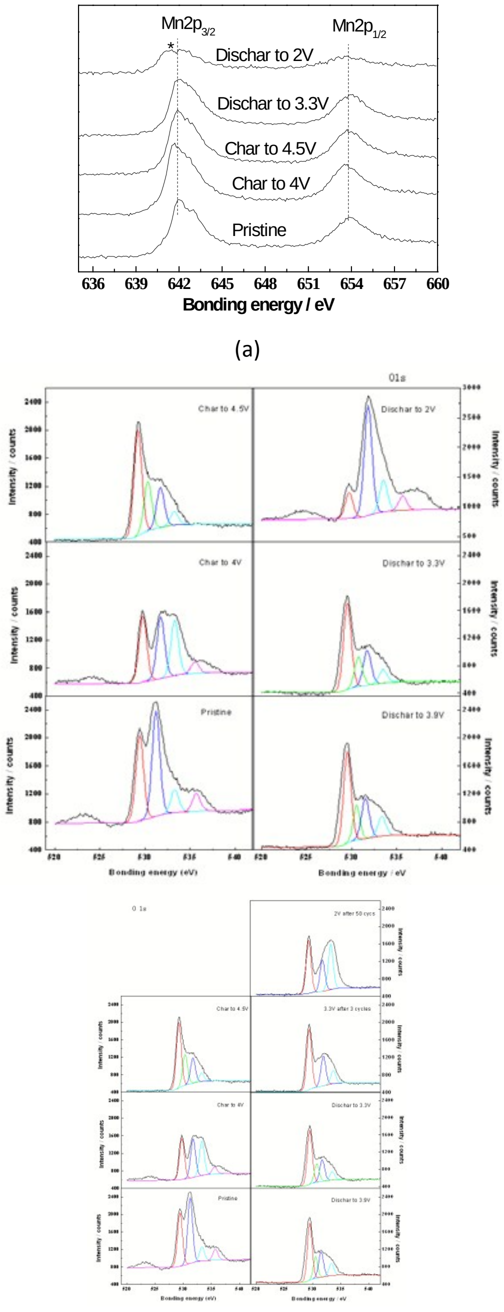


Fig.2 charge and discharge profiles and cycle stability of P3-$Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ (a: 10 mA g^{-1} between 3.5 and 4.5 V; b: 15 mA g^{-1} between 2 and 4.5 V)



(a)

(b)

Fig.3 XPS patterns of Mn and O during the initial charge and discharge process (a: Mn2p; b: O1s)

XPS probes the electronic states at surface atoms. Fig. 3a shows Mn 2p XPS patterns of of P3-$Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$ at five different states of initial cycle. There is little change in the Mn XPS peaks between 3.3 and 4.5 V on charge and discharge. whereas For O 1s, five states of the first cycle and two cycled states are checked, and it can be found in Fig. 3b that the oxygen XPS peaks show dramatic changes that are not observed with layered oxides having *3d* redox energies above the O-*2p* bands [2-4].

Fig. 4 compares the *ex situ* XRD patterns of nominal *P3*-$Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ of a dried as-prepared electrode with those taken after charge to 4 and 4.5 V, discharge to 3.9, 3.3, and 2.0 V and after 5 cycles between 3.5 and 4.5 V as well as after 50 cycles between 2.0 and 4.5 V. The *P3* structure is retained after all treatments with no evidence of the O3 (Na in octahedral coordination) or other phases. The initial charge capacity of 128 mAh g^{-1} between 3.5 and 4.5 V corresponds to extraction of 0.44 Na^+ per formula unit, which leaves 0.16 Na^+/f.u. to stabilize the *P3* structure. It is remarkable that after 50 cycles in the voltage ranges 2.0 to 4.5 V versus Na^0, the XRD peaks retain the as-prepared structure with no shift of the lattice parameter. The only change is the intensity of the XRD peaks of the cycled sample and a broadening of some peaks. The *P3* structure remains stable over electrochemical cycling even though oxidation on charge introduces holes primarily in the O-*2p* bands. This observation suggests formation of an amorphous second phase grows with cycling.

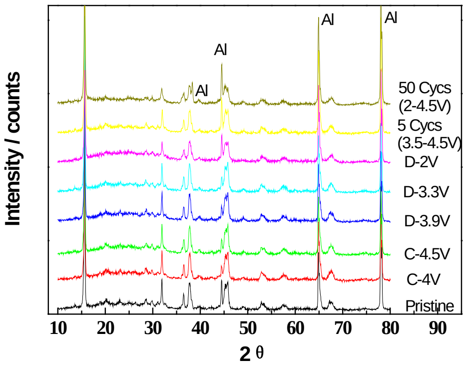


Fig.4 Ex situ XRD patterns of P3- $Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ at different states

Table 1 The change of Li and Na during cycles

	Li	Na	Mn	(Li+Na)/Mn
As prepared	0.2000	0.6158	0.800	1.0197/1
1st	0.1895	0.6042	0.800	0.9921/1
2nd	0.1789	0.5896	0.800	0.9606/1
10th	0.1686	0.5848	0.800	0.9417/1
20th	0.1329	0.5762	0.800	0.8864/1
50th	0.0546	0.5051	0.800	0.6997/1

Since the oxidation of the O-*2p* band over the long plateau of the *V-I* curves must be accomplished by loss of Na^+ and/or Li^+, we determined the loss of Li and Na relative to that of Mn after different numbers of cycles (between 2 and 4.5 V). The results are listed in Table 1 where it is seen that the alkali ions are not fully returned after each cycle. After cycling, some Li^+ were found in the electrolyte and on the surface of the electrode. The loss of alkali ions would be charge-compensated by the formation of peroxide anions, $(O_2)^{2-}$, in an amorphous surface phase that grows on cycling. The capacity corresponds to the removal of 0.44 Na^+ per formula unit and the ratio (Li + Na)/Mn = 0.7 after 50 cycles corresponds to 0.56 A^+ per formula unit in the Na^+ planes. Therefore, the capacity can still be retained after 50 cycles as indicated in Fig. 2(b).

Conclusions

The data presented indicate that the Mn(V)/Mn(IV) redox energy lies sufficiently far below the top of the O-*2p* bands that, on oxidation, holes are introduced into the O-*2p* bands with retention of the *P3* structure. However, a strong fade of the voltage plateau with cycling of nominal $Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ in a Na half-cell shows that the holes introduced into the O-*2p* bands are not cycled reversibly and may become trapped in peroxide ions within an amorphous phase. The difference in the voltage profiles of Fig. 2(a) and 2(b) reflect a higher surface oxidation of the oxide at the faster rate of charge.

Acknowledgements

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Broader Context

A transition-metal oxide with a redox near the top of the O-$2p^6$ bands has a large admixture of cation *d* and O-*2p* in the states at the top of the valence band. As the energy of the cation redox couple moves from above to below the top of the O-$2p^6$ bands, the states at the top of the valence bond change from primarily cation-*d* to primarily O-*2p*. The optimal O-*2p* character to catalyze the oxygen-evolution reaction (OER) has yet to be determined. In the case of the octahedral-site Mn(IV) cation in an oxide, the energy of the Mn(V)/Mn(IV) couple lies sufficiently below the top of the valance bond that the states are primarily O-*2p* and the Mn(V) valence state is not accessible. Nevertheless, reversible oxidation of the Mn(IV) oxides is possible to a limited extent; the states at the top of the valance band have a dominant O-*2p* character that leads to a facile formation of peroxide ions with the evolution of oxygen gas, O_2. As a result, α - MnO_2 is a good catalyst for the OER, but with the layered oxide of this report, oxidation of the primarily O-$2p^6$ valence band introduces an amorphous surface layer in which peroxide ions$(O_2)^{2-}$, may be formed reversibly.

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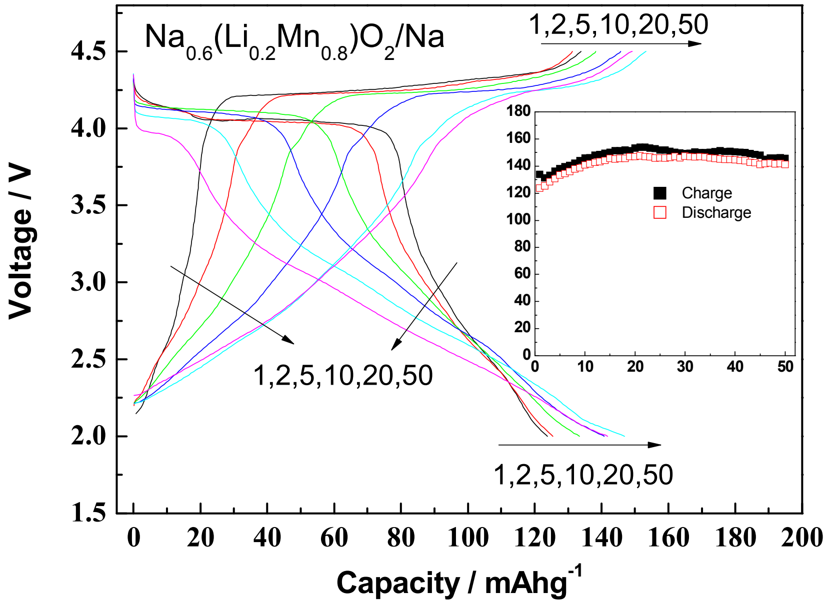

Oxidation of layered P3-$Na_{0.6}(Li_{0.2}Mn_{0.8})O_2$ by electrochemical removal of Na^+ introduces holes into the O-*2p* bands at 4.2 V, but the voltage plateau fades on cycling.