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In operando X-ray absorption spectroscopy study of charge rate effects on the atomic environment in graphene-coated Li-rich mixed oxide cathode

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ABSTRACT

Li_2O extraction from the electrode material is known to be a dominant mechanism of irreversible battery capacity loss in the first cycle. The extraction mechanism of the Li^+ ions shows dependence on the charge rate. Here for the first time we report the difference in the electrochemical behavior at two different charge rates (0.125 C vs 0.5 C) observed using novel design transmission coin cells in the graphene-coated $Li(Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ cathode by *in operando* X-ray absorption spectroscopy (XAS). The results obtained from Mn, Co, and Ni atom XANES/EXAFS demonstrate that, whilst during fast charge Li_2O extraction is localized to the lithium slab in the crystal structure, the delithiation is deeper at the slower charge rate, when Li^+ ions are removed from both the transition metal and lithium layers. In the slow charge cell, Ni—O bond splitting resulting from the Jahn-Teller distortion were clearly identified at approximately 4.224 V when a sudden rise in the bond length was observed in the EXAFS analysis of Mn—O and Co—O bonds. The results demonstrate the power of using the novel cell design for transmission *in operando* XAS.

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1. Introduction

Much interest has been aroused in the lithium-rich Mn-based composites as active materials for high capacity lithium-ion batteries. These systems described by the chemical formula $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Mn, Co, Ni) continue to have immense appeal as portable energy sources ranging from mobile devices to electric vehicles. The cathode of the active material benefits from high theoretical reversible capacity (over 250 mAh g^{-1}), good structural/thermal stability, high discharge capacity, and lower cost [1–10]. The lithium-rich Mn-based cathode that contains different transition metals, e.g. $Li(Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ offers advantages over compositions containing a single transition metal [11–18]. Both economical and ecological considerations lead to the use of transition metal composites as cathode materials. A major factor limiting the performance of the lithium-rich Mn-based cathode is the large irreversible capacity loss of 40–100 mAh g^{-1} during the first electrochemical cycle [19–23]. Li^+ ion extraction accompanied by oxygen release is known to be the dominant mechanism of the irreversible capacity loss [20,24–27]. A key factor for delivering high charge capacity in the

lithium-rich systems is the structural integration of the two distinct crystallographic phases found in these systems, Li_2MnO_3 (monoclinic, $C2/m$) and $LiMO_2$ (trigonal, $R\bar{3}m$), where M denotes a transition metal ion (Mn, Ni or Co). At the crystal level, the structure of the composite can be visualised by the interleaving of close-packed layers from the two compounds, namely the (001) planes from Li_2MnO_3 and the (003) planes from $LiMO_2$ with the interlayer spacing of ~4.7 Å, which allows the intimate integration of the two crystallographic components at the atomic level [3,28]. At the electrochemical level, this mixed metal oxide cathode material exhibits the two-phase reaction plateau around 4.4 V in the galvanostatic profile during initial charge.

The $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ cathode is composed of two main layers, namely, lithium-ion layer at 3a sites and transition metal layer at 3b sites that comprise a trigonal structure as illustrated in Fig. 1.

Li^+ not only occupies the lithium-layer in the $R\bar{3}m$, it can also partially occupy the transition metal layer in the $C2/m$ structure [25,26,28]. The lithium-ion surrounded by Mn^{4+} in the transition metal layer of $C2/m$ produces cation ordering which forms the Li_2MnO_3 structure [25,26,28]. It has been also proposed that the Li_2MnO_3 phase directly affects the electrochemical property and stability of the cathode [26,28, 29]. Therefore, on the one hand Li_2MnO_3 contributes to the battery performance, but is also the main factor that leads to the capacity fading during electrochemical cycling. The removal of oxygen vacancies from
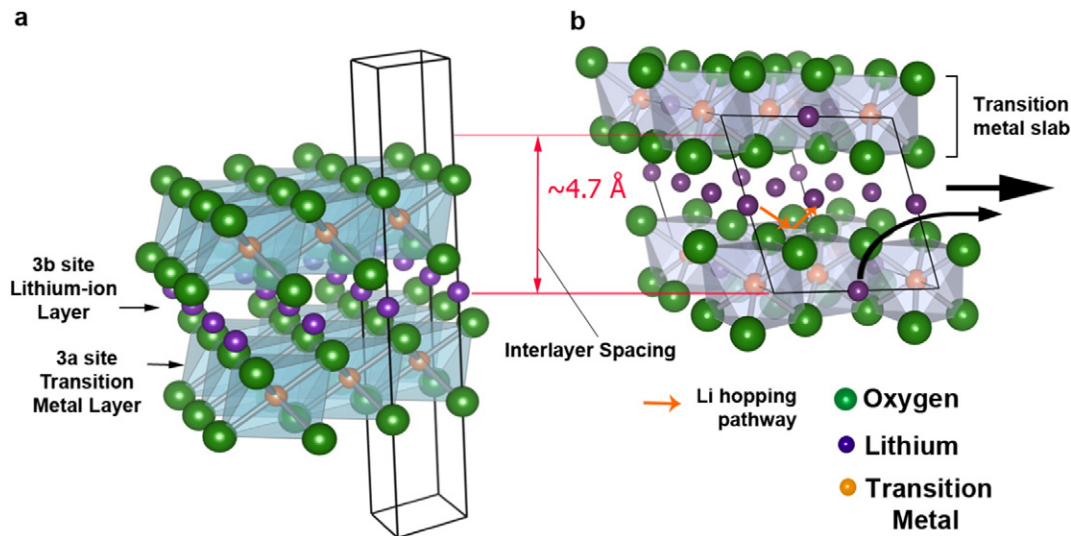
Fig. 1. Crystal structure of (a) LiMO$_2$ (trigonal, $R\bar{3}m$) and (b) Li$_2$MnO$_3$ (monoclinic, $C2/m$). Due to the presence of the interlayer spacing (~4.7 Å), the crystal structure can be combined in an integrated composite. Black arrows indicates the extraction of the lithium-ions. In principle, Li$^+$ must be deintercalated from lithium layer and TM-layer either continuously or simultaneously during charge.

the crystal lattice during the first charge reduces the number of available sites for Li$^+$ (de)intercalation [20,27,28]. This process is followed by the migration of the transition metals from the surface into the bulk of the active material [20,30,31]. It is likely that both the removal of oxygen vacancies and the migration of transition metal ions during the first charge lead to the irreversible capacity loss in the lithium-ion batteries of this type.

In lithium-rich layered oxides, Li$^+$ ion mobility has become a central issue that needs to be elucidated to understand the performance and to improve the stability of the cathode. The mechanism of lithium mobility in the crystal structure is usually explained by the Li$^+$ hopping mechanism between octahedral sites via an intermediate tetrahedral site [32, 33]. An ab initio modelling study by Kang and Cedar suggests [32,33]

that the Li slab spacing and the electrostatic repulsion between Li$^+$ and transition metals (Mn, Co, and Ni) determine the Li$^+$ mobility in the layered oxide structure. In this computation model, the activation barrier for the Li$^+$ diffusion decreases with the Li slab spacing. Li$^+$ mobility is highly sensitive to the distance between the oxygen layers (Fig. 1). The electrostatic repulsion between Li$^+$ and the transition metal ions at the tetrahedral sites is another major factor that affects the Li$^+$ mobility in the crystal structure [32]. Importantly, it is not only the presence of the transition metals at tetrahedral sites, but also their oxidation states that affect the mobility. Lower oxidation states result in weaker electrostatic interaction with the diffusing Li$^+$ ion [32]. It has been also suggested that the cation mixing influences the Li$^+$ mobility [34–37]. It is therefore likely that the atomic-local environment
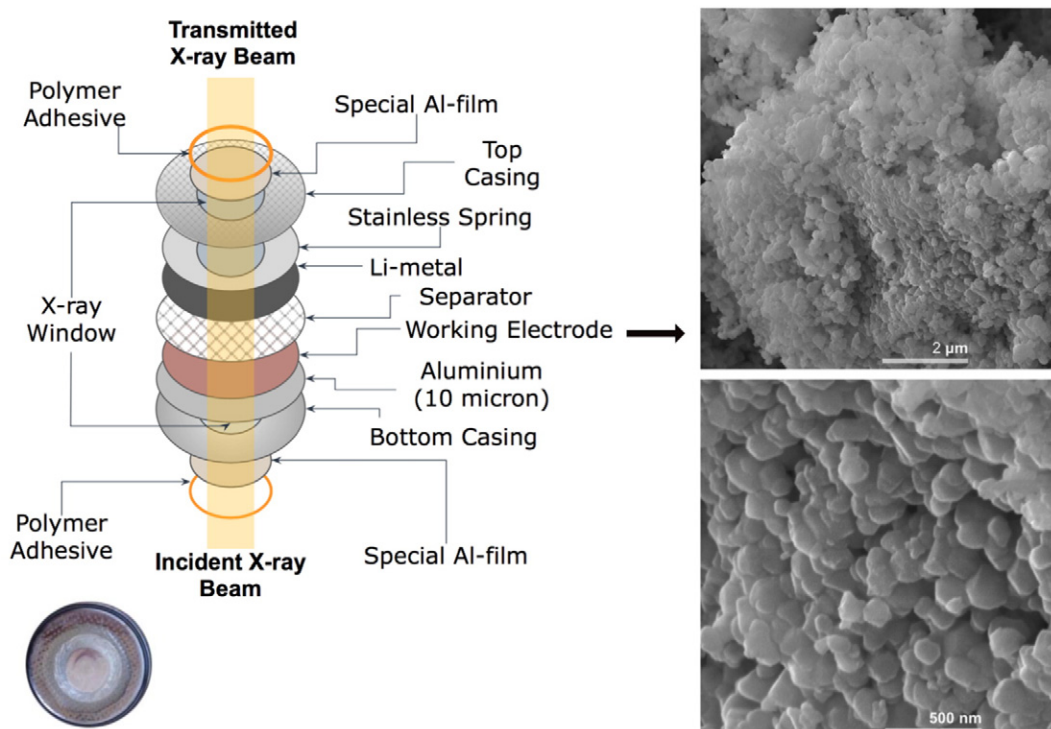

Fig. 2. Illustration of *in operando* cell design. Scanning Electron Microscopy of graphene-coated Li(Li$_{0.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$)O$_2$ cathode.