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# Revealing of the Activation Pathway and Cathode Electrolyte Interphase Evolution of Li-Rich 0.5Li<sub>2</sub>MnO<sub>3</sub>·0.5LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> Cathode by in Situ Electrochemical Quartz Crystal Microbalance

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Supporting Information



ABSTRACT: The first-cycle behavior of layered Li-rich oxides, including Li<sub>2</sub>MnO<sub>3</sub> activation and cathode electrolyte interphase (CEI) formation, significantly influences their electrochemical performance. However, the Li<sub>2</sub>MnO<sub>3</sub> activation pathway and the CEI formation process are still controversial. Here, the first-cycle properties of  $xLi_2MnO_3(1-x)$  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$  (x = 0, 0.5, 1) cathode materials were studied with an in situ electrochemical quartz crystal microbalance (EQCM). The results demonstrate that a synergistic effect between the layered  $Li_2MnO_3$  and  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$  structures can significantly affect the activation pathway of Li1.2Ni0.12Co0.12Mn0.56O2, leading to an extra-high capacity. It is demonstrated that Li<sub>2</sub>MnO<sub>3</sub> activation in Li-rich materials is dominated by electrochemical decomposition (oxygen redox), which is different from the activation process of pure  $Li_2MnO_3$  governed by chemical decomposition ( $Li_2O$  evolution). CEI evolution is closely related to Li<sup>+</sup> extraction/insertion. The valence state variation of the metal ions (Ni, Co, Mn) in Li-rich materials can promote CEI formation. This study is of significance for understanding and designing Li-rich cathode-based batteries.

KEYWORDS: Li-rich materials, Li<sub>2</sub>MnO<sub>3</sub> activation, oxygen redox, CEI evolution, in situ EQCM

# **1. INTRODUCTION**

Continuing interest in sustainable use of Li-ion batteries (LIBs) for electrical transportation is driving further developments in cathode materials. Layered Li-rich oxide cathode materials exhibit high specific capacity of more than 250 mAh  $g^{-1}$  and, thus, are considered as potential candidates for the next-generation LIBs.<sup>1,2</sup> Nevertheless, commercial applications of Li-rich cathode materials are hindered by three main drawbacks. First, a large irreversible capacity loss happens in the first charge-discharge process. Second, their cyclability and rate capability are not sufficient. Third, significant voltage decay occurs during cycling.<sup>3-5</sup> All these issues are highly related to the first-cycle charge-discharge processes. Therefore, a better understanding and further controlling of the first-

cycle processes of the Li-rich oxide cathode will be beneficial to improve its electrochemical properties.

Li<sub>2</sub>MnO<sub>3</sub> activation and cathode electrolyte interphases (CEI) formation/dissolution are two key reactions of Li-rich oxides in the first cycle. Many studies have been done to understand the activation process of Li2MnO3 and CEI evolution. However, there is no consensus on the  $\rm Li_2MnO_3$  activation process.<sup>6-11</sup> For example, it was claimed that O<sup>2-</sup> was oxidized to an  $O_2^{2^-}$  species or  $O_2^{2^-}$ -like localized electron holes on oxygen ("oxygen redox") during Li<sub>2</sub>MO<sub>3</sub> (M = Ru,

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Sn, Mn) activation.<sup>6–9</sup> In contrast, other studies show very different  $\text{Li}_2\text{O}$  evolution processes.<sup>10,11</sup> So far, most results were achieved using ex situ electron paramagnetic resonance, X-ray photoelectron spectroscopy,<sup>6</sup> resonant inelastic X-ray scattering,<sup>7</sup> in situ Raman spectroscopy,<sup>9,10</sup> and wavelength dispersive spectroscopy.<sup>11</sup> However, an important limitation of these experimental studies is that only surface information can be obtained.<sup>6,7,9–11</sup>

Electrochemical quartz crystal microbalance (EQCM) is able to detect in real time the mass change of a bulk electrode with high sensitivity during electrochemical processes.<sup>12–14</sup> For example, EQCM was used as a gravimetric probe to detect concentration and compositional changes of microporous activated carbons.<sup>12</sup> EQCM was also adapted to analyze formation of electrode/electrolyte interphase on graphite and Sn thin film electrodes.<sup>15,23</sup> CEI formation on the Li-rich  $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$  surface was also studied by EQCM, but the relationship between the reaction in Lirich electrodes and CEI formation was not clarified.<sup>25</sup>

There are two different activation pathways that can lead to mass loss of Li-rich cathode materials, namely electrochemical decomposition (oxygen redox)<sup>6-9</sup> and chemical decomposition (Li<sub>2</sub>O evolution).<sup>10,11</sup> The mass loss can be used as a criterion to differentiate the decomposition processes because electrochemical decomposition leads to Li<sup>+</sup> deintercalation from electrode, whereas no Li<sup>+</sup> deintercalation occurs during chemical decomposition. In this study, we applied in situ EQCM to investigate the first-cycle charge-discharge processes of Li12Ni012Co012Mn056O2 (0.5Li2MnO3.0.5Li-Ni<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>), Li<sub>2</sub>MnO<sub>3</sub>, and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> electrode materials. We found that the activation pathway of Li<sub>2</sub>MnO<sub>3</sub> in Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> is influenced by synergistic effects between Li<sub>2</sub>MnO<sub>3</sub> and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>. Our results show that the Li<sub>2</sub>MnO<sub>3</sub> activation in Li-rich material is dominated by electrochemical decomposition (oxygen redox), as opposed to activation of pure Li<sub>2</sub>MnO<sub>3</sub>, which is governed by chemical decomposition (Li<sub>2</sub>O evolution). CEI formation is evidently affected by changes in the valence states of metal ions in Li-rich material. Our study has deepened the understanding of the first-cycle behavior of Li-rich materials, which will be helpful for designing Li-rich cathode-based batteries.

## 2. EXPERIMENTAL SECTION

**2.1. Materials Preparation and Characterization.** A modified Pechini method was adopted to prepare  $Li_2MnO_3$ , Li- $Ni_{0.3}Co_{0.3}Mn_{0.4}O_2$ , and  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  materials, as reported in our previous study.<sup>16</sup> Citric acid, dissolved in ethylene glycol in a 1:4 molar ratio, was used as the chelating agent. Then, a metal ion solution containing a stoichiometric amount of Li-(CH<sub>3</sub>COO)·H<sub>2</sub>O (an excess of 5% in molar ratio), Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, and Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was added dropwise. A clear solution was obtained after heating at 90 °C while stirring for 1 h. The resulting solution was further heated at 140 °C to esterify and evaporate the excess water. The residue was vacuum dried in an oven at 180 °C for 12 h for thermal polymerization to yield an organic polymer foam. The obtained precursor was preheated at 450 °C for 6 h, and then calcined at 700 °C for 24 h.

The microstructure and crystal structure were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and powder X-ray diffraction (XRD, Philips X'Pert Pro), respectively. XRD measurements were run over the  $2\theta$  range of  $15^{\circ}-90^{\circ}$ . The scan rate was  $1^{\circ}$  min<sup>-1</sup>. XRD refinement was conducted by the Rietveld method using the Topas program (Bruker, Topas 4.2).

2.2. EQCM Measurements. A slurry composed of 80 wt % cathode materials, 10 wt % acetylene black, and 10 wt %

polyvinylidenediuoride (PVDF) in N-methylpyrrolidone was prepared and dripped on the Au-coated AT-cut 7.995 MHz 1 inch diameter quartz crystal surface. Before use, the Au-coated crystal was rinsed with ethanol and acetone for 10 min each, respectively. The loaded active material was controlled at  $4.5 \pm 0.5 \ \mu$ g. Under this mass load, the quartz crystal can maintain a resonance oscillation ( $\Delta f/f_0$  < 2%.  $\Delta f$  is the mass change of the load, and  $f_0$  is resonance frequency of the Au crystal).<sup>17,23</sup> The mass of each material was obtained from the difference between the resonance frequency of the Au-coated crystal with and without active material. The geometric area of the Au electrode was 0.196 cm<sup>2</sup>. The prepared quartz crystal was dried at 80 °C for 12 h in vacuum. After cooling down, it was fixed on the crystal holder and used as the working electrode. Figure S1a,b shows an optical micrograph of a Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> slurry-coated quartz crystal after drying at 80 °C for 12 h in vacuum and an optical micrograph of the Li12Ni012Co012Mn056O2 slurry surface. The loaded material is distributed uniformly in the center of the Au crystal.

**2.3. EQCM Measurements.** EQCM measurements were conducted using a three-electrode system at 25 °C. Figure 1 shows



Figure 1. Schematic diagram of electrochemical quartz crystal microbalance (EQCM) experimental setup.

a schematic diagram of the EQCM setup. Both the reference and the counter electrode are lithium strips. The electrochemical cell assembly was operated in an argon-filled glove box at room temperature. LiPF<sub>6</sub> (LP, 1 M) dissolved in ethylene carbonate/dimethyl carbonate (EC:DMC = 1:1 v/v) was used as the electrolyte. For each EQCM test, the volume of the electrolyte was 0.8 mL. Cyclic voltammetry (CV)-EQCM tests were conducted by a CHI440C EQCM work-station (CH Instruments) and its accessories. For this equipment, a 1 Hz frequency increase means a 1.34 ng weight decrease. Before the CV-EQCM tests, the three-electrode system was kept standing for 6 h to reach steady state. CV curves were generated between 2.0 and 4.8 V with a scanning rate of 0.2 mV s<sup>-1</sup>. The mass change of the working electrodes was recorded by the EQCM during the CV measurements.

When  $\Delta f/f_0 < 2\%$ , the mpe (mass accumulated per mole of electron transferred) values were estimated according to the Sauerbrey equation (eq 1) and Faraday's law (eq 2),<sup>17,23</sup>

$$\Delta m = -\frac{A(\mu_{q}\rho_{q})^{0.5}\Delta f}{2f_{0}^{2}} = -C_{f} \cdot \Delta f$$
(1)

mpe = 
$$nF \cdot \frac{\Delta m}{Q} = -nC_f F \frac{\Delta f}{Q}$$
 (2)

where  $\Delta m$  is the mass change,  $\Delta f$  is the change in resonance frequency,  $f_0$  is the fundamental resonance frequency (7.995 MHz), A is the surface area of the electrode (0.196 cm<sup>2</sup>),  $\mu_q$  is the shear modulus of quartz (2.947 × 10<sup>11</sup> g cm<sup>-1</sup> s<sup>-2</sup>),  $\rho_q$  is the density of quartz (2.684 g cm<sup>-3</sup>),  $C_f$  is the sensitivity factor for this setup (1.34 ng·Hz<sup>-1</sup>), Q is the charge passed through the electrode in Coulombs, F is the Faraday constant (96485 C mol<sup>-1</sup>), and n is the valence number of the ion.

However, the Sauerbrey equation always needs a correction related to the electrode/electrolyte interface. Another factor that affects the frequency shift is the change of density ( $\rho_L$ ) and viscosity ( $\eta_L$ ) of the electrolyte in contact with the quartz crystal electrode, <sup>16,26</sup> as follows



Figure 2. SEM images of (a)  $Li_2MnO_3$ , (b)  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$ , and (c)  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$ ; (d) XRD patterns for the three samples; (e) initial charge–discharge profiles at 0.1 C, and (f) CV curves for the first cycle of  $Li_2MnO_3$ ,  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$ , and  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$ . The scan rate of CV curves is 0.2 mV s<sup>-1</sup>.

$$\Delta f_{\eta\rho} = -f_0^{3/2} \left[ \frac{\Delta(\eta_{\rm L}\rho_{\rm L})}{\pi \mu_{\rm q} \rho_{\rm q}} \right]^{1/2}$$
(3)

The observed frequency change,  $\Delta f$ , is the sum of the frequency change associated with mass loss/gain ( $\Delta f_{\rm m}$ ) and the change in ( $\eta_{\rm L}\rho_{\rm L}$ ) during the electrochemical process

$$\Delta f = \Delta f_{\rm m} + \Delta f_{\eta\rho} \tag{4}$$

 $\Delta(\eta_L\rho_L)$  can be estimated from the change in the resistance of the quartz crystal  $(\Delta R)$ 

$$\Delta R = \left[2\pi f_0 \Delta(\eta_{\rm L} \rho_{\rm L})\right]^{1/2} A/k^2 = -\left[\pi (2\mu_{\rm q} \rho_{\rm q})^{1/2} A/(k^2 f_0)\right] \Delta f_{\eta\rho}$$
(5)

where k is an electromechanical factor. From eq 5, we see that  $\Delta f_{\eta\rho}$  has a negative linear correlation with  $\Delta R$ . However, due to the inhomogeneous concentration of the electrolyte near the electrode during the charge–discharge process (including density and viscosity,  $\eta_{\rm L}\rho_{\rm L}$ ),  $\Delta R$  is also affected by roughness of the electrode, which changes when strong deposition reaction occurs, such as electrolyte decomposition at <2.6 V region.<sup>26</sup> It is difficult to arrive at an accurate quantitative relationship between  $\Delta R$  and  $\Delta f_{\eta\rho}$ . In this work, we used  $\Delta R$  to do a qualitative correction of obtained  $\Delta f$  from tests. An increase of  $\Delta R$  means a decrease of  $\Delta f_{n\rho}$ .

2.4. Electrochemical Measurements. CR2025-type coin cells were used to measure the electrochemical performance. A mixture of the synthesized material, polyvinylidenediuoride (PVDF) binder, and acetylene black in a weight ratio of 8:1:1 soaked in N-methyl-2pyrrolidone solvent was coated on a 16 mm diameter Al foil current collector to prepare the electrode. The electrodes were dried at 100 °C for 12 h in vacuum before each test. The weight of the active material in each electrode was kept at  $1.25 \pm 0.1$  mg cm<sup>-2</sup>. An argonfilled glove box was used to assemble the CR2025-type coin cells. Lithium foils and Celgard 2400 film were used as the counter electrode and separator, respectively. LiPF<sub>6</sub> (1 M)/EC/DMC (EC:DMC = 1:1 v/v,  $H_2O$  concentration < 5 ppm) was used as the electrolyte. A Land-V34 battery tester (Wuhan, China) was used for galvanostatic control of the cells, which were kept at 30 °C. The current density of 1 C equals to 200 mA  $g^{-1}$ . Capacities were calculated based on the weight of the active material. A ChI660E work station was used to do the cyclic voltammetry test. All materials were tested between 2.0 and 4.8 V (vs Li/Li<sup>+</sup>) at a scan rate of 0.2 mV s<sup>-1</sup>.

Electrochemical impedance spectroscopy was performed on a VSP multichannel potentiostatic-galvanostatic system (VERSASTATV3, USA). The electrode potential was increased stepwise from open circuit voltage to 4.8 V and then decreased to 2.0 V with 0.1-0.2 V potentiostatic steps. Before EIS tests at each potential, the voltage was kept constant for 20 min. The impedance spectra were recorded by applying an AC voltage of 5 mV in the frequency range from 1 mHz to 5 MHZ.

## 3. RESULTS AND DISCUSSION

3.1. Microstructure, Crystal Structure, and Electrochemical Performance. Figure 2a-c shows SEM images of Li<sub>2</sub>MnO<sub>3</sub>, LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>, and Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>. All samples have similar microstructures, but the particle sizes are different. The  $Li_2MnO_3$  and  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$ particles were between 100 and 200 nm, whereas those of  $\rm LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$  ranged from 200 and 300 nm. XRD profiles are displayed in Figure 2d. All three samples have distinct features indicating a layered structure. For Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>, the strong peaks at  $18.7^{\circ}$  and  $44.6^{\circ}$  can be indexed to (003) and (104) planes of the  $\alpha$ -NaFeO<sub>2</sub> parent hexagonal structure ( $R\overline{3}m$ symmetry). Li<sub>2</sub>MnO<sub>3</sub> exhibits a monoclinic structure with strong peaks at  $18.6^{\circ}$  and  $44.7^{\circ}$ , which correspond to (001) and (131) planes of space group C2/m.<sup>9</sup> Both Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> and Li<sub>2</sub>MnO<sub>3</sub> have a broad superlattice (110) peak at  $20^{\circ}$ – $25^{\circ}$ , which indicates cation ordering in the transition-metal layer and stacking faults formed during materials preparing process.9 Figure S2 shows the refinement XRD patterns of Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>.

The calculated ratio of  $Li_2MnO_3$  and  $LiMO_2$  (M = Ni, Co, Mn) is 48.9:51.1, which is very close to 50:50. Considering the calculation error, it is acceptable to denote the Li-rich material as  $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$ . More detailed structure information of  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  can be seen in our previous study.<sup>16</sup>

Figure 2e displays the initial charge–discharge profiles of  $Li_2MnO_3$ ,  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$ , and  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  at 0.1 C. For  $Li_2MnO_3$ , only a voltage plateau above 4.4 V is observed during charge.<sup>10</sup> Instead of a very stable plateau at



Figure 3. (a) CV curve for first cycle and the simultaneous EQCM response of  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$ ; plots of  $\Delta f$  vs  $\Delta Q$  for  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  (b) during anodic scanning and (c) cathodic scanning; (d) plots of  $\Delta R_{CEI}$  versus *E* (potential) for  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  at different potentials during the first charge–discharge process, and the equivalent circuit model for EIS measurements is in the inset.

Table 1. Mass Change and mpe Values Measured from the EQCM Data for Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> During First Cycle<sup>a</sup>

			charge	discharge					
potential region (V)	3.7-4.0	4-4.2	4.2-4.4	4.4-4.65	4.65-4.8	4.8-4.1	4.1-3	3-2.6	2.6-2
$\Delta f$ -pure LP (Hz)	-1.91	-1.461	-1.88	-4.51	-8.02	1.26	2.42	-0.45	-6.97
$\Delta f$ (Hz)	67.27	60.86	22	102.6	-6.2	29.3	-102.5	-79.65	-310.8
$\Delta m$ (ng)	-90.14	-81.55	-29.48	-137.48	8.31	-39.26	137.35	106.73	416.4
$\Delta m/m_1$ (%)	-2.12	-1.92	-0.69	-3.23	0.19	-0.92	3.22	2.51	9.78
mpe (g mol <sup>-1</sup> )	-32.23	-19.72	-6.03	-12.85	0.42	-1.39	25.33	34.94	53.42
$\Delta R$	~0	~0	~0	~0	1	1	1	1	↑
7		/			-				

<sup>a</sup>The Frequency Change of Pure LiPF<sub>6</sub>/EC + DMC (LP) electrolyte was given as Comparison. The mass of loaded  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  material  $m_1$  is 4.258  $\mu$ g.

 ${\sim}4.5$  V, the inclined plateau is attributed to the low conductivity of pure  ${\rm Li_2MnO_3.}^{10,28}$  During discharge, the voltage declines rapidly, showing a capacity of only 126.8 mAh  $g^{-1}$ . The irreversible capacity ratio (ICR), defined as irreversible capacity divided by charge capacity, was 48.85%. During charge, LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> has a voltage plateau above 3.7 V, corresponding to  $Ni^{2+}/Ni^{4+}$  and  $Co^{3+}/Co^{4+}$  redox couples. It has a discharge capacity of 178.7 mA h  $g^{-1}$  and an 18.92% ICR. Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> has a capacity of 120 mAh  $g^{-1}$  during the initial charge process, which is associated with the Ni<sup>2+</sup>/Ni<sup>4+</sup> and Co<sup>3+</sup>/Co<sup>3.6+</sup> redox couples.<sup>9,17</sup> The plateau above 4.4 V corresponding to Li<sub>2</sub>MnO<sub>3</sub> activation is observed and provides an additional capacity of 200 mAh  $g^{-1}$ . Upon discharging, Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> exhibits a sloping voltage curve and has a capacity of 244.7 mAh g<sup>-1</sup> with a 22.56% ICR. The discharge capacity of Li<sub>12</sub>Ni<sub>012</sub>Co<sub>012</sub>Mn<sub>056</sub>O<sub>2</sub> is much higher than the average of Li<sub>2</sub>MnO<sub>3</sub> and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>, indicating a synergistic effect between Li<sub>2</sub>MnO<sub>3</sub> and the layered structure in the Lirich oxide material. Lim et al. have proved that layered LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> benefits from the structural stability of Li<sub>2</sub>MnO<sub>3</sub>.<sup>18</sup> However, the explanation for why extra capacity results from the introduction of Li<sub>2</sub>MnO<sub>3</sub> into layered LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> is unclear.

The CV profiles (for the first cycle) of Li<sub>2</sub>MnO<sub>3</sub>, LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> and Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> are shown in Figure 2f. For Li<sub>2</sub>MnO<sub>3</sub>, no anodic peak emerges until ~4.4 V. The current peak between 4.4 and 4.8 V is attributed to Li<sub>2</sub>MnO<sub>2</sub> activation and simultaneous lithium extraction. A small reductive current peak can be observed below 3.6 V corresponding to Mn<sup>4+</sup>/Mn<sup>3+</sup> reduction. The anodic and cathodic current densities of Li<sub>2</sub>MnO<sub>3</sub> are distinctly smaller than those of LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> and Li12Ni012C0012Mn056O2. For LiNi03C003Mn04O2, the first peak between 3.65 and 4.3 V during charge corresponds to Ni<sup>2+</sup>/Ni<sup>4+</sup> and Co<sup>3+</sup>/Co<sup>3.6+</sup> redox couples. The second smaller peak at ~4.5 V is due to the  $Co^{3.6+}/Co^{4+}$  redox couple.<sup>17</sup> A reduction peak centered at  $\sim 3.7$  V is observed, which is attributed to Ni<sup>4+</sup>/Ni<sup>2+</sup> and Co<sup>4+</sup>/Co<sup>3+</sup> redox couples. Below 3.0 V, no peak is observed, which indicates no  $Mn^{3+}$  formation. The CV profile of Li12Ni012Co012Mn056O2 shows anodic peaks between 3.65 and 4.4 V for the  $Ni^{2+}/Ni^{4+}$  and  $Co^{3+}/$ Co<sup>3.6+</sup> redox couples.<sup>17</sup> The subsequent oxidation peak from 4.4 to 4.8 V is due to Li<sub>2</sub>MnO<sub>3</sub> activation and lithium extraction, which is similar to that of Li2MnO3. During reduction, the Ni<sup>4+</sup>/Ni<sup>2+</sup> and Co<sup>4+</sup>/Co<sup>3+</sup> redox peaks at  $\sim$ 3.8 V resemble LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>.<sup>5</sup>

**3.2. First-Cycle Interfacial Properties.** Figure 3a displays the first cycle CV curve and the simultaneous EQCM response

of  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$ . The corresponding  $\Delta f - \Delta Q$  (charge) plots are shown in Figure 3b,c. To help interpret these observations, analogous data for pure LiPF<sub>6</sub>/EC + DMC, without loaded materials, are depicted in Figure S3.

The diagrams of  $\Delta R$  versus *E* (electrode potential) of pure LiPF<sub>6</sub>/EC + DMC electrolyte, Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>, LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>, and Li<sub>2</sub>MnO<sub>3</sub> during the first CV cycle are shown in Figure S4.

In many regions, the variation of  $\Delta R$  is negligible (~0), so the Sauerbrey equation is still valid, which is similar to Tsai's and Wu's reports.<sup>14,20</sup> For example, in the 4.4–4.65 V region during the first anodic scanning of Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>, Li<sub>2</sub>MnO<sub>3</sub> activation occurs and the variation of  $\Delta R$  is near zero. In many other regions, the variation of  $\Delta R$  is not so obvious, so the mass loss/gain is the main process affecting the shift in frequency ( $\Delta f$ ). In this study, we first calculated the mass changes and mpe values by the Sauerbrey equation, and then we analyzed and adjusted the mpe values with  $\Delta R$ . The obtained values of these parameters are listed in Table 1.

Figures 2e and 3a illustrate that the capacity, current, and  $\Delta f$ are all very small between the open circuit potential (OCP) and 3.7 V during the first charge. Changes in this region are attributed mainly to absorption/desorption of electrolyte molecules or ions.<sup>27</sup> In the first charge,  $\Delta R$  is almost zero when the potential is below 4.65 V, which suggests that the Sauerbrey equation is valid in this region. It is observed that the measured mpe is close to 7 g  $mol^{-1}$  (which is the atomic weight of Li) in the 4.2-4.4 V region, which indicates delithiation of Li^+ along with  $Ni^{2+}/\widetilde{Ni}^{4+}$  and  $Co^{3+}/Co^{3.6+}$ oxidation reactions.<sup>19</sup> However, the mpe values in 3.7-4.2 and 4.4-4.65 V are higher than 7 g mol<sup>-1</sup>, indicating additional processes. For analyzing the formation/dissolution of CEI,  $\Delta R_{\text{CEI}}-E$  plots at different potential during the first charge are displayed as a red line in Figure 3d. The corresponding Nyquist plots are shown in Figure S5a-d. The equivalent circuit, shown as an insert in Figure 3d, was applied to analyze the EIS data. In this equivalent circuit,  $R_{\rm S}$ represents the internal resistance of the battery,  $R_{CEI}$  and  $C_{CEI}$ represent the resistance and capacitance of the CEI film, while  $R_{\rm ct}$  and  $C_{\rm dl}$  represent the charge-transfer resistance and doublelayer capacitance. W is the Warburg impedance related to Li<sup>+</sup> diffusion.<sup>21</sup> The fitted impedance parameters are listed in Table S1. There is always a native surface film on most cathode surfaces ( $Li_2CO_3$  on lithium transition-metal oxides).<sup>22</sup> This is the source of  $R_{CEI}$  in the initial state. It can be seen that the  $R_{\text{CEI}}$  decreases with the potential increase in the 3.7–4.2 V region, which indicates the dissolution of the CEI layer. There is always HF in the electrolyte. Native Li<sub>2</sub>CO<sub>3</sub> can react with HF and lead to dissolution.<sup>24</sup> Electrochemical decomposition of Li<sub>2</sub>CO<sub>3</sub> was also reported by a previous study.<sup>27</sup> Hence, the Li<sub>2</sub>CO<sub>3</sub> degradation is a possible pathway of CEI dissolution, which can make the measured mpe value higher. This is consistent with the high mpe value in the 3.7-4.2 V region. In the 4.4-4.65 V region, R<sub>CEI</sub> increases slightly, indicating the new CEI film produced. Therefore, the mass change is attributed to the irreversible decomposition of the Li<sub>2</sub>MnO<sub>3</sub> component in  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  and to CEI formation. Figure S3 further confirms the above analysis. The decreased  $\Delta f$  during charge indicates no gold base dissolution (increased  $\Delta f$ ), which means gold is stable in the LiPF<sub>6</sub>/EC + DMC electrolyte. The  $\Delta f$  variance is originated from electrolyte reactions. For the pure LiPF<sub>6</sub>/EC + DMC electrolyte, the absorption/desorption process of electrolyte molecules/ions

occurs in the OCP-4 V region. In the 4–4.65 V region, it can be observed from the CV curve that the electrolyte begins to oxidize. Frequency decrease and negligible  $\Delta R$  can also be seen, corresponding to a mass increase and indicating that the CEI layer derived from the electrolyte has formed. CEI formation can reduce the calculated mpe value. In the 3.7–4.2 V region of Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>, the native CEI layer dissolved. But the mpe value in the 4–4.2 V region is smaller than that in 3.7–4 V, which is attributed to new CEI film formation derived from the electrolyte. Between 4.2 and 4.4 V, the mpe value is slightly smaller than 7 g mol<sup>-1</sup>, which is also attributed to new CEI formation. In the 4.4–4.65 V region, the mass change is attributed to the irreversible decomposition of Li<sub>2</sub>MnO<sub>3</sub> component in Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> and to CEI formation.

There have been many studies about the decomposition of  $\text{Li}_2\text{MnO}_3$ , and  $\text{O}_2^{2-}$  (true species or localized electron holes on oxygen). Li<sub>2</sub>O was proved to be formed in different research.<sup>6-10</sup> The specific reactions may follow as eq 6 and eq 7.

$$2Li_2MnO_3 \to 4Li^+ + O_2^{2-} + 2MnO_2 + 2e^-$$
(6)

$$\text{Li}_{2}\text{MnO}_{3} \rightarrow \text{Li}_{2}\text{O} + \text{MnO}_{2} \tag{7}$$

For eq 6, two electrons are transferred and four Li<sup>+</sup> ions are extracted. The mpe value of eq 6 is  $28/2 = 14 \text{ g mol}^{-1}$ , and Li<sup>+</sup> extraction can lead to mass loss. For eq 7, no electrons are transferred and no species are lost from the material, so the mass change of eq 7 is zero. As can be seen in Table 4, the maximum of mass loss of Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> in the 4.4-4.65 V region is 277.4 ng, when eq 6 is the only reaction. However, the real mass loss is 137.5 ng, which is 49.57% of the maximal mass loss originating from Li<sub>2</sub>MnO<sub>3</sub> activation. Considering that CEI film formation leads to mass gain, and chemical decomposition according to eq 7 does not affect the mass, electrochemical decomposition according to eq 6 is the main process of Li<sub>2</sub>MnO<sub>3</sub> activation for Li-rich oxide  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2.$  The measured mpe value in the 4.4–4.65 V region is 12.85 g mol<sup>-1</sup>, which is slightly smaller than 14 for eq 6. CEI film formation leads to a mass gain for the electrode, but no electrons transfer of electrode material, and makes the measured mpe value smaller, which is consistent with our experiment. In the region above 4.65 V, the  $\Delta R$  is slightly increased, and a further oxidation reaction of the electrolyte occurs because of the high charge voltage.

Figure 3c illustrates the  $\Delta f - \Delta Q$  plot during the first discharge process, and the corresponding mass change and mpe values are listed in Table 1.  $\Delta R$  increases during the first discharge, which leads to a negative shift of frequency. Thus, the actual shift of frequency caused by the mass gain is smaller than that observed in Figure 2c, and the real mpe value is smaller than that listed in Table 1. In the 4.8-4.1 V region, a continuous oxidation reaction of the electrolyte occurs. In the region below 2.6 V, a decomposition reaction of the electrolyte occurs, which is consistent with the very small capacity in the charge-discharge curve, as demonstrated in Figure 2e. Considering the previous reports and our experimental data (mpe = 53.42,  $\Delta R$  increase), Li<sub>2</sub>CO<sub>3</sub> (mpe = 37) is one of the possible products.<sup>10,28</sup> In these two regions, there are no valence state changes for the metal ions in  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_{2,}$  and the interfacial reactions for  ${\rm Li}_{1.2}{\rm Ni}_{0.12}{\rm Co}_{0.12}{\rm Mn}_{0.56}{\rm O}_2$  and pure electrolyte are very similar. In the 4.1–2.6 V region, the insertion of Li<sup>+</sup> causes the mass to



Figure 4. CV curve for first cycle and the simultaneous EQCM response of (a)  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$  and (b)  $Li_2MnO_3$ ; plots of  $\Delta f$  vs  $\Delta Q$  for  $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$  (c) during anodic scanning and (e) during cathodic scanning; plots of  $\Delta f$  vs  $\Delta Q$  for  $Li_2MnO_3$  (d) during anodic scanning and (f) during cathodic scanning.

Table 2. Mass Change and mpe Values Measured From the EQCM Data for LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> During First Cycle<sup>4</sup>

	charge						discharge				
potential region (V)	3.65-3.9	3.9-4.1	4.1-4.4	4.4-4.53	4.53-4.65	4.65-4.8	4.8-4.1	4.1-3.9	3.9-3	3-2.6	2.6-2
$\Delta f$ (Hz)	42.45	134.44	132.2	44.9	19.3	21.7	6.2	-38.7	-117	-45.9	-288.7
$\Delta m$	-57.15	-180.1	-177.1	-60.2	-25.86	-29.1	-8.3	51.9	156.8	61.5	386.8
$\Delta m/m_2$ (%)	-1.36	-4.28	-4.21	-1.43	-0.61	-0.69	-0.20	1.23	3.73	1.46	9.19
mpe (g mol <sup>-1</sup> )	-8.46	-56.5	-38.62	-6.73	-2.92	-1.6	-0.24	61.4	20.1	30.8	53.4
$\Delta R$	~0	↑	$\downarrow$	~0	~0	1	1	↑	1	1	1
<sup>a</sup> The mass of loaded	LiNi <sub>0.3</sub> Co <sub>0.3</sub>	Mn <sub>0.4</sub> O <sub>2</sub> m	aterial m <sub>2</sub> is	s 4.209 μg.							

increase. However, the mpe value in the 4.1-2.6 V region is higher than 7 g mol<sup>-1</sup>, indicating that the insertion of Li<sup>+</sup> maybe not be the only electrochemical process. However, considering the shift of frequency caused by  $\Delta R$ , more proof should be given. The blue line in Figure 3d displays the  $\Delta R_{\text{CEI}} - E$  plot of Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> at different potentials during the first discharge. The corresponding Nyquist plots are shown in Figure S5e,f, and the fitted impedance parameters are listed in Table S2. It is observed that  $R_{CEI}$  increases as the potential decreases in the 4.1–2.6 V region. Considering that the mpe value is greater than 7 g  $mol^{-1}$ , a new CEI film with lower conductivity has apparently formed in this region. For pure  $LiPF_6/EC + DMC$  electrolyte, the frequency change is slightly higher in the 4.1–2.6 V region. Considering that an increase in  $\Delta R$  leads to negative shift of frequency; the measured frequency increase implies CEI dissolution and mass loss. The difference between the pure electrolyte and Li12Ni012Co012Mn056O2 is attributed to the valence state changes of metal ions in this region, as the interfacial reactions are very similar when there are no valence

state changes of metal ions in the region above 4.1 V and below 2.6 V.  $\,$ 

To further clarify the interfacial property of Li-rich Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> material, the interfacial properties of layered LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> and pure Li<sub>2</sub>MnO<sub>3</sub> were also investigated for comparison. As demonstrated in Figure 4a, the CV curve during the first cycle and the simultaneous EQCM response of LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> can be observed. The corresponding  $\Delta f - \Delta Q$  plots are shown in Figure 4c,e. Table 2 summarizes the mass change and mpe values during the first cycle. As with Li12Ni012Co012Mn056O2, electrolyte absorption/desorption occurs below 3.65 V. The mpe value in the 3.65–3.9 V region is near 7 g mol<sup>-1</sup> and  $\Delta R$  is insignificant, which indicates delithiation along with Ni<sup>2+</sup>/Ni<sup>4+</sup> and Co<sup>3+</sup>/ Co<sup>3.6+</sup> oxidation. In the 3.9–4.4 V region,  $\Delta R$  increases slightly, whereas the mpe value varies. The large mpe values indicate that dissolution of the native CEI layer is the dominated process, as with Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>. When the potential is above 4.4 V, the variation of  $\Delta R$  is near zero and the Sauerbrey equation is applicable. In the 4.4-4.53 V

Table 3. Mass Char	ge and mpe `	Values Measured	From the EQC	M Data for Li <sub>2</sub> MnO	3 During First Cycle
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	charge					discharge					
potential region (V)	OCP-3.8	3.8-4.05	4.05-4.4	4.4-4.65	4.65-4.75	4.75-4.8	4.8-3.9	3.9-3.3	3.3-3	3-2.6	2.6-2
$\Delta f$ (Hz)	-29.34	3.06	-30.66	5.34	-13.94	-5.65	42.81	-6.79	-5.28	-4.18	-196.5
$\Delta m$ (ng)	39.3	-4.1	41.08	-7.16	18.68	7.57	-57.36	9.1	7.07	5.6	263.27
$\Delta m/m_3$ (%)	0.82	-0.09	0.86	-0.15	0.39	0.16	-1.20	0.19	0.15	0.12	5.51
mpe (g mol <sup>-1</sup> )	58.96	-8.45	21.34	-1.51	4.31	2.37	-2.69	16.74	7.55	3.34	50.12
$\Delta R$	↑	1	~0	~0	1	1	~0	$\downarrow$	~0	↑	~0
<sup><i>a</i></sup> The mass of loaded	Li <sub>2</sub> MnO <sub>2</sub> m	aterial m <sub>2</sub> is	4.777 ug								

region, Co<sup>3.6+</sup>/Co<sup>4+</sup> oxidation reactions occur along delithiation.<sup>17</sup> The mpe value in the 4.4-4.53 V region is 6.73 g  $mol^{-1}$ , which is slightly smaller than 7 g  $mol^{-1}$ . This result demonstrates that Li<sup>+</sup> extraction along with Co<sup>3.6+</sup>/Co<sup>4+</sup> oxidation are the main processes in this region. Nyquist plots of LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> shown in Figure S6 also illustrate that  $R_{CEI}$  is slightly increased, indicating that there is new CEI film formed. When the voltage is higher than 4.65 V, electrolyte oxidation occurs. For the first discharge of Li- $Ni_{0.3}Co_{0.3}Mn_{0.4}O_2$ , it is very similar to that of Li-rich  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$ .  $\Delta R$  increases during the first discharge, as with Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>. Continuous electrolyte oxidation occurs in the 4.8-4.1 V region, and the electrolyte is decomposed when the potential is below 2.6 V. Between 4.1 and 2.6 V, Li<sup>+</sup> insertion is accompanied by metal ion reduction and CEI film formation.

Figure 4b shows the CV curve for the first cycle and the simultaneous EQCM response of Li2MnO3. The corresponding  $\Delta f - \Delta Q$  (charge) plots are displayed in Figure 4d,f. Table 3 summarizes the mpe value during the first cycle. For the  $Li_2MnO_3$  electrode,  $\Delta R$  increases when the voltage is below 3.8 V but hardly varies when the potential is above 3.8 V. There is no obvious electrochemical reaction besides the absorption/desorption of electrolyte molecule/ion when the potential is below 3.8 V. In the 3.8-4.05 V region, the native CEI film dissolves, as with the case of Li-rich material. In the region between 4.05 and 4.4 V, new CEI is produced. In the 4.4-4.65 V region, the Sauerbrey equation is valid and the decomposition of Li<sub>2</sub>MnO<sub>3</sub> is the dominant reaction. As displayed in Table 4, the mass of loaded  $Li_2MnO_3$  is 4.777  $\mu g$ . The maximum extracted  $Li^+$  is 567.589 ng when eq 6 is the only decomposition pathway. However, the real mass loss of Li<sub>2</sub>MnO<sub>3</sub> is only 7.959 ng, which is only 1.4% of the maximal

Table 4. Comparison of Mass Changes and mpe Value of  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  and  $Li_2MnO_3$  Materials in 4.4–4.65 V Region

	$\begin{array}{c} Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2\\ (0.5Li_2MnO_3\Delta0.5LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2)\end{array}$	Li <sub>2</sub> MnO <sub>3</sub>
mass of loading	4.258	4.777
active material $(\mu g)$		
mass ratio of Li <sup>+</sup>	9.774%	11.882%
the maximum of mass change of Li <sup>+</sup> extraction (ng)	-416.164	-567.589
the maximum of mass change of Li <sub>2</sub> MnO <sub>3</sub> activation (ng)	-277.442	-567.589
the real mass change in 4.4–4.65 V region (ng)	-137.484	-7.959
mpe	-12.65	-1.51

mass loss from  $Li_2MnO_3$  activation and much smaller than 49.57% of Li-rich oxide. The mpe value is 1.51 g mol<sup>-1</sup>, which is distinctly smaller than the 14 g mol<sup>-1</sup> of eq 6. This result indicates that the CEI film formed. Considering that the new CEI film formation can counter some of the mass loss, we conclude that a chemical decomposition of  $Li_2MnO_3$  to  $Li_2O$  and  $MnO_2$  is the dominant reaction, as shown in eq 7, which coincides with the electrochemical results in Figure 2f.

However, electrochemical decomposition is the main process of the Li<sub>2</sub>MnO<sub>3</sub> component in Li-rich oxide Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub>. The obviously different routes of Li<sub>2</sub>MnO<sub>3</sub> decomposition reactions in the same potential region demonstrate that there is a synergistic effect between Li<sub>2</sub>MnO<sub>3</sub> (C2/m) and the layered structure ( $R\overline{3}m$ ) in Li-rich oxide material, which is in accordance with the first charge–discharge profiles in Figure 2e. Pure chemical decomposition does not contribute to capacity. Therefore, the different decomposition pathway of Li<sub>2</sub>MnO<sub>3</sub> in Li-rich oxides is the reason why Li-rich oxides can provide higher capacity than pure Li<sub>2</sub>MnO<sub>3</sub> and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> materials.

The first discharge of pure Li<sub>2</sub>MnO<sub>3</sub> is also very similar to that of Li-rich oxide, where electrolyte oxidation occurs in the 4.8–3.9 V region and the electrolyte is decomposed for potentials below 2.6 V. In the region between 3.9 and 2.6 V, Li<sup>+</sup> inserts into the electrode and CEI is formed. However, there is some difference. The mpe value is much smaller than that of Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> and LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>, indicating that changes in the valence state of Ni<sup>4+</sup> and Co<sup>4+</sup> have a bigger effect on CEI formation than those of Mn<sup>4+</sup> and O<sub>2</sub><sup>2-</sup>.

Scheme 1a demonstrates the EQCM working principle in this work. The Li<sup>+</sup> insertion/extraction and CEI evolution occurring on the electrodes lead to mass change, which can be measured by the frequency change of the crystal quartz. The CV curves can also be recorded, which can be used to calculate the charge evolution during the test. Combining the mass change and charge evolution, we can get the mpe value, which is closely related with different kinds of reactions and important to determine what reactions occur in different potential regions, such as Li<sub>2</sub>MnO<sub>3</sub> activation in the 4.4-4.65 V region during the first charge. Scheme 1b illustrates the proposed interfacial reaction mechanism of Li-rich oxides during the first charge, based on the previous results in this article. Solvated electrolyte ions adsorb on the surface of the electrode in the initial period. Subsequently, Li<sup>+</sup> extracts from material. When the potential is below 4.4 V,  $Ni^{2+}$  and  $Co^{3+}$  are oxidized to Ni<sup>4+</sup> and Co<sup>3.6+</sup> to compensate for the Li<sup>+</sup> extraction. Native CEI dissolution takes place at the same time. In the voltage region between 4.4 and 4.65 V, Li<sub>2</sub>MnO<sub>3</sub> activation and new CEI formation occurs. At higher potentials, electrolyte oxidation is the dominant reaction. Detailed reactions in the Li<sub>2</sub>MnO<sub>3</sub> activation region of Li-rich oxides Scheme 1. (a) Diagram Showing the EQCM Working Principle in This Work; (b) Proposed Main Interfacial Reaction Mechanisms During First Charge and (c) Detailed Reactions in the Li<sub>2</sub>MnO<sub>3</sub> Activation Voltage Region of Li-rich Oxides and Pure Li<sub>2</sub>MnO<sub>3</sub>; (d) Proposed Main Interfacial Reaction Mechanisms During First Discharge



and pure Li<sub>2</sub>MnO<sub>3</sub> are depicted in scheme 1c. For pure Li<sub>2</sub>MnO<sub>3</sub>, the activation process is mainly chemical decomposition to Li<sub>2</sub>O and MnO<sub>2</sub>. However, for Li-rich oxides, electrochemical decomposition to Li<sup>+</sup>,  $O_2^{2-}$ , and MnO<sub>2</sub> is the dominant pathway. The proposed main interfacial reaction mechanism of Li-rich oxides during the first discharge is illustrated in Scheme 1d. Continuous electrolyte oxidation occurs at the high voltage. After the voltage dropping to 4 V, Li<sup>+</sup> insertion accompanied by metal ion and  $O_2^{2-}$  reduction subsequently occurs, while CEI forms in the same time. When the voltage is below 2.6 V, electrolyte decomposition is the main process.

#### 4. CONCLUSIONS

In summary, we investigated the Li<sub>2</sub>MnO<sub>3</sub> activation pathway and CEI formation/dissolution of  $xLi_2MnO_3\Delta(1-x)$ - $LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2$  (x = 0, 0.5, 1) cathode materials in 1 M LiPF<sub>6</sub>/EC + DMC by in situ EQCM and EIS. A synergistic effect between layered Li2MnO3 and LiNi03Co03Mn04O2 components that explains the extra-high capacity for the  $Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$  cathode was found. The synergistic effect in Li-rich  ${\rm Li}_{1.2}{\rm Ni}_{0.12}{\rm Co}_{0.12}{\rm Mn}_{0.56}{\rm O}_2$  cathodes can affect the activation pathway of the Li<sub>2</sub>MnO<sub>3</sub> component in Li-rich material. Specifically, the activation of pure Li2MnO3 is governed by chemical decomposition to Li<sub>2</sub>O. However, Li<sub>2</sub>MnO<sub>3</sub> activation in Li-rich material is dominated by electrochemical activation to  $O_2^{2-}$  (oxygen redox). Chemical decomposition does not contribute to the electrode capacity because there is no delithiation. This explains why Li-rich materials (0.5Li<sub>2</sub>MnO<sub>3</sub>·0.5LiNi<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>) have a higher capacity than the mean value of Li<sub>2</sub>MnO<sub>3</sub> and Li-Ni<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub>.

Besides activation of Li-rich materials, it has been observed that CEI formation/dissolution accompanies Li<sup>+</sup> extraction/ insertion. We also found that changes in the valence state of metal ions (Ni, Co, Mn) in Li-rich material can promote CEI formation. Focusing on reducing chemical decomposition during first-cycle activation, and controlling the promotion of metal ions valence states changes should provide a route to improve the electrochemical performance of Li-rich materials.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b02236.

I m p e d a n c e p a r a m e t e r s of L i - r i c h Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> at different potentials during first cycle; optical micrograph of Li-rich material-coated EQCM electrode; refinement XRD patterns of Li-rich material; CV-EQCM test data of pure LiPF<sub>6</sub>/EC + DMC electrolyte without loaded materials; evolution of resistance ( $\Delta R$ ) of pure electrolyte, Li-rich, layered oxide and Li<sub>2</sub>MnO<sub>3</sub> during first cycle; EIS results of Li-rich Li<sub>1.2</sub>Ni<sub>0.12</sub>Co<sub>0.12</sub>Mn<sub>0.56</sub>O<sub>2</sub> at different potentials during first cycle; and EIS results of layered Li-Ni<sub>0.3</sub>Co<sub>0.3</sub>Mn<sub>0.4</sub>O<sub>2</sub> during first charge (PDF)

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#### Notes

The authors declare no competing financial interest.

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