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Revealing of the Activation Pathway and Cathode Electrolyte Interphase Evolution of Li-Rich $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ Cathode by in Situ Electrochemical Quartz Crystal Microbalance

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1 **Revealing of the Activation Pathway and Cathode Electrolyte Interphase Evolution of Li-rich**
2 **$0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ Cathode by In-Situ Electrochemical Quartz Crystal**
3 **Microbalance**

4
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1 **Abstract**

2 The first-cycle behavior of layered Li-rich oxides, including Li_2MnO_3 activation and cathode
3 electrolyte interphase (CEI) formation, significantly influences their electrochemical performance.
4 However, the Li_2MnO_3 activation pathway and the CEI formation process are still controversial.
5 Here, the first-cycle properties of $x\text{Li}_2\text{MnO}_3 \cdot (1-x) \text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ ($x = 0, 0.5, 1$) cathode
6 materials were studied with an in-situ electrochemical quartz crystal microbalance (EQCM). The
7 results demonstrate that a synergistic effect between layered Li_2MnO_3 and $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$
8 structures can significantly affect the activation pathway of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$, leading to an
9 extra-high capacity. It is demonstrated that Li_2MnO_3 activation in Li-rich materials is dominated by
10 electrochemical decomposition (oxygen redox), which is different from the activation process of pure
11 Li_2MnO_3 governed by chemical decomposition (Li_2O evolution). CEI evolution is closely related to
12 Li^+ extraction/insertion. The valence state variation of the metal ions (Ni, Co, Mn) in Li-rich material
13 can promote CEI formation. This study is of significance for understanding and designing Li-rich
14 cathode-based batteries.

15
16 **Key words:** Li-rich materials, Li_2MnO_3 activation, oxygen redox, CEI evolution, in-situ EQCM

17

1 **1. Introduction**

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

12 Li₂MnO₃ activation and cathode electrolyte interphases (CEI) formation/dissolution are two key
13 reactions of Li-rich oxides in the first cycle. Many previous studies have been done to understand the
14 activation process of Li₂MnO₃ and CEI evolution. However, there is no consensus on the Li₂MnO₃
15 activation process.⁶⁻¹¹ For example, it was claimed that O²⁻ was oxidized to an O₂²⁻ species or
16 O₂²⁻-like localized electron holes on oxygen (“oxygen redox”) during Li₂MO₃ (M =Ru, Sn, Mn)
17 activation.⁶⁻⁹ In contrast, other studies show very different Li₂O evolution processes.¹⁰⁻¹¹ So far,
18 most results were achieved using ex-situ electron paramagnetic resonance (EPR), X-ray
19 photoelectron spectroscopy (XPS),⁶ resonant inelastic X-ray scattering (RIXS),⁷ in-situ Raman,⁹⁻¹⁰
20 and wavelength dispersive spectroscopy (WDS)¹¹. However, an important limitation of these
21 experimental studies is that only surface information can be obtained.^{6-7,9-11}

1 Electrochemical quartz crystal microbalance (EQCM) is able to detect in real time the mass
2 change of a bulk electrode with high sensitivity during electrochemical processes.¹²⁻¹⁴ For example,
3 EQCM was used as a gravimetric probe to detect concentration and compositional changes of
4 microporous activated carbons.¹² EQCM was also adapted to analyze formation of
5 electrode/electrolyte interphase on graphite and Sn thin film electrodes.^{15,23} CEI formation on the
6 Li-rich $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2$ surface was also studied by EQCM, but the
7 relationship between reaction in Li-rich electrodes and CEI formation was not clarified.²⁵

8 There are two different activation pathways that can lead to mass loss of Li-rich cathode
9 materials, namely electrochemical decomposition (oxygen redox)⁶⁻⁹ and chemical decomposition
10 (Li_2O evolution)¹⁰⁻¹¹. The mass loss can be used as a criterion to differentiate the decomposition
11 processes because electrochemical decomposition leads to Li^+ de-intercalation from electrode while
12 no Li^+ de-intercalation occurs during chemical decomposition. In this study, we applied in-situ
13 EQCM to investigate the first-cycle charge-discharge processes of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$
14 ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$), Li_2MnO_3 and $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ electrode materials. We
15 found that the activation pathway of Li_2MnO_3 in $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ is influenced by
16 synergistic effects between Li_2MnO_3 and $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$. Our results show that the Li_2MnO_3
17 activation in Li-rich material is dominated by electrochemical decomposition (oxygen redox), as
18 opposed to activation of pure Li_2MnO_3 , which is governed by chemical decomposition (Li_2O
19 evolution). CEI formation is evidently affected by changes in the valence states of metal ions in
20 Li-rich material. Our study has deepened the understanding of the first-cycle behavior of Li-rich
21 materials, which will be helpful for designing Li-rich cathode-based batteries.

22

1 **2. Experimental**

2 **2.1. Materials Preparation and Characterization**

3 A modified Pechini method was adopted to prepare Li_2MnO_3 , $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and
4 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ materials, as reported in our previous study.¹⁶ Citric acid, dissolved
5 in ethylene glycol in a 1:4 molar ratio, was used as chelating agent. Then a metal ion solution
6 containing a stoichiometric amount of $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ (an excess of 5% in molar ratio),
7 $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ was added dropwise.
8 A clear solution was obtained after heating at 90 °C while stirring for 1 h. The resulting
9 solution was further heated at 140 °C to esterify and evaporate the excess water. The residue
10 was vacuum dried in an oven at 180 °C for 12 h for thermal polymerization to yield an
11 organic polymer foam. The obtained precursor was pre-heated at 450 °C for 6 h, and then
12 calcined at 700 °C for 24 h.

13 The microstructure and crystal structure were characterized by scanning electron microscope
14 (SEM, Hitachi S-4800) and powder X-ray diffraction (XRD, Philips X'Pert Pro), respectively. XRD
15 measurements were run over the 2θ range of 15-90°. The scan rate was 1 °min⁻¹. XRD refinement
16 was conducted by Rietveld method using Topas program (Bruker, Topas 4.2).

17

18 **2.2. EQCM Measurements**

19 (1) Preparation of materials modified quartz crystal electrode

20 Slurry composed of 80 wt. % cathode materials, 10 wt. % acetylene black and 10 wt. % PVDF
21 in N-methylpyrrolidone was prepared and dripped on the Au-coated AT-cut 7.995 MHz 1 inch
22 diameter quartz crystal surface. Prior to use, the Au-coated crystal was rinsed with ethanol and

1 acetone for 10 min each, respectively. The loaded active material was controlled at $4.5 \pm 0.5 \mu\text{g}$.
2 Under this mass load, the quartz crystal can maintain a resonance oscillation ($\Delta f/f_0 < 2\%$. Δf is
3 the mass change of the load, and f_0 is resonance frequency of Au crystal).^{17,23} The mass of each
4 material was obtained from the difference between the resonance frequency of the Au-coated crystal
5 with and without active material. The geometric area of the Au electrode was 0.196 cm^2 . The
6 prepared quartz crystal was dried at $80 \text{ }^\circ\text{C}$ for 12 h in vacuum. After cooling down, it was fixed on
7 the crystal holder and used as the working electrode. Fig S1a and b shows an optical micrograph of a
8 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ slurry-coated quartz crystal after drying at $80 \text{ }^\circ\text{C}$ for 12 h in vacuum and an
9 optical micrograph of the $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ slurry surface. The loaded material is distributed
10 uniformly in the center of Au crystal.

11 (2) Details of measurements

12 EQCM measurements were conducted using a three-electrode system at $25 \text{ }^\circ\text{C}$. Fig 1 shows a
13 schematic diagram of the EQCM setup. Both the reference and the counter electrode are lithium
14 strips. The electrochemical cell assembly was operated in an argon-filled glove box at room
15 temperature. 1 M LiPF_6 (LP) dissolved in ethylene carbonate/dimethyl carbonate (EC: DMC = 1:1
16 v/v) was used as the electrolyte. For each EQCM test, the volume of electrolyte was 0.8 mL .
17 CV-EQCM tests were conducted by a CHI440C EQCM workstation (CH Instruments) and its
18 accessories. For this equipment, a 1 Hz frequency increase means a 1.34 ng weight decrease. Before
19 the CV-EQCM tests, the three-electrode system was kept standing for 6 h to reach steady state. CV
20 curves were generated between 2.0 V to 4.8 V with a scanning rate of 0.2 mV s^{-1} . The mass change
21 of the working electrodes was recorded by the EQCM during the CV measurements.

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

$$3 \quad \Delta m = -\frac{A(\mu_q \rho_q)^{0.5} \Delta f}{2f_0^2} = -C_f \cdot \Delta f \quad (1)$$

$$4 \quad mpe = nF \cdot \frac{\Delta m}{Q} = -nC_f F \frac{\Delta f}{Q} \quad (2)$$

5 where Δm is the mass change, Δf is the change in resonance frequency, f_0 is the fundamental
 6 resonance frequency (7.995 MHz), A is the surface area of the electrode (0.196 cm²), μ_q is
 7 the shear modulus of quartz (2.947*10¹¹ g·cm⁻¹·s⁻²), ρ_q is the density of quartz (2.684 g cm⁻³),
 8 C_f is the sensitivity factor for this setup (1.34 ng·Hz⁻¹), Q is the charge passed through the
 9 electrode in Coulombs, F is the Faraday constant (96485 C mol⁻¹), and n is the valence
 10 number of the ion.

11 However, the Sauerbrey equation always needs a correction related to the
 12 electrode/electrolyte interface. Another factor that affects the frequency shift is the change of
 13 density (ρ_L) and viscosity (η_L) of the electrolyte in contact with the quartz crystal
 14 electrode,^{16,26} as follows

$$15 \quad \Delta f_{\eta\rho} = -f_0^{\frac{3}{2}} \left[\frac{\Delta(\eta_L \rho_L)}{\pi \mu_q \rho_q} \right]^{\frac{1}{2}} \quad (3)$$

16 The observed frequency change Δf is the sum of the frequency change associated with mass
 17 loss/gain (Δf_m) and the change in ($\eta_L \rho_L$) during the electrochemical process:

$$18 \quad \Delta f = \Delta f_m + \Delta f_{\eta\rho} \quad (4)$$

19 $\Delta(\eta_L \rho_L)$ can be estimated from the change in the resistance of the quartz crystal (ΔR),

$$20 \quad \Delta R = [2\pi f_0 \Delta(\eta_L \rho_L)]^{1/2} A/k^2 = -[\pi(2 \mu_q \rho_q)^{\frac{1}{2}} A/(k^2 f_0)] \Delta f_{\eta\rho} \quad (5)$$

21 where k is an electromechanical factor. From eq 5, we see that $\Delta f_{\eta\rho}$ has a negative linear
 22 correlation with ΔR . However, due to the inhomogeneous concentration of electrolyte near

1 electrode during charge-discharge process (including density and viscosity, $\eta_L\rho_L$), and the
2 ΔR is also affected by roughness of electrode, which changes when strong deposition
3 reaction occurs, such as electrolyte decomposition at < 2.6 V region.²⁶ It is difficult to make
4 an accurate quantitatively relationship between ΔR and $\Delta f_{\eta\rho}$. In this work, we used ΔR to
5 do a qualitative correction of obtained Δf from tests. An increase of ΔR means a decrease
6 of $\Delta f_{\eta\rho}$.

8 **2.3. Electrochemical Measurements**

9 CR2025-type coin cells were used to measure the electrochemical performance. A mixture of
10 the synthesized material, polyvinylidenediufioride (PVDF) binder and acetylene black at a weight
11 ratio of 8: 1: 1 soaked in N-methyl-2-pyrrolidone (NMP) solvent was coated on a 16 mm diameter Al
12 foil current collector to prepare the electrode. The electrodes were dried at 100 °C for 12 h in
13 vacuum before each test. The weight of active material in each electrode was kept at 1.25 ± 0.1 mg
14 cm^{-2} . An argon-filled glove box was used to assemble the CR2025-type coin cells. Lithium foils and
15 Celgard 2400 film were used as counter electrode and separator, respectively. 1 M $\text{LiPF}_6/\text{EC}/\text{DMC}$
16 (EC: DMC = 1:1 v/v, H_2O concentration < 5 ppm) was used as the electrolyte. A Land-V34 battery
17 tester (Wuhan, China) was used for galvanostatic control of the cells, which were kept at 30 °C.
18 The current density of 1 C equals to 200 mA g^{-1} . Capacities were calculated based on the weight of
19 active material. A CHI660E work station was used to do cyclic voltammetry test. All the materials
20 were tested between 2.0 and 4.8 V (vs. Li/Li^+) at a scan rate of 0.2 mV s^{-1} .

21 Electrochemical impedance spectroscopy (EIS) was performed on a VSP multichannel
22 potentiostatic-galvanostatic system (VERSASTATV3, USA). The electrode potential was increased

1 stepwise from open circuit voltage (OCP) to 4.8 V and then decreased to 2.0 V with 0.1-0.2 V
2 potentiostatic steps. Before EIS tests at each potential, the voltage was kept constant for 20 mins.
3 The impedance spectra were recorded by applying an AC voltage of 5 mV in the frequency range
4 from 1 MHz to 5 mHz.

6 **3. Results and Discussion**

7 **3.1 Microstructure, crystal structure and electrochemical performance**

8 Fig 2a-c shows SEM images of Li_2MnO_3 , $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. All
9 the samples have similar microstructures, but the particle sizes are different. The Li_2MnO_3 and
10 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ particles were between 100 and 200 nm, while those of $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$
11 ranged from 200 and 300 nm. XRD profiles are displayed in Figure 2d. All of these three samples
12 have distinct features indicating a layered structure. For $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and
13 $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$, the strong peaks at 18.7° and 44.6° can be indexed to (003) and (104) planes of
14 the $\alpha\text{-NaFeO}_2$ parent hexagonal structure ($R\bar{3}m$ symmetry). Li_2MnO_3 exhibits monoclinic structure
15 with strong peaks at 18.6° and 44.7° , which correspond to (001) and (131) planes of space group
16 $C2/m$.⁹ Both $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and Li_2MnO_3 have a broad superlattice (110) peak at $20\text{-}25^\circ$,
17 which indicates cation ordering in the transition-metal layer and stacking faults formed during
18 materials preparing process.⁹ Fig S2 shows the refinement XRD patterns of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$.
19 The calculated ratio of Li_2MnO_3 and LiMO_2 (M = Ni, Co, Mn) is 48.9:51.1, which is very close to
20 50:50. Considering the calculation error, it is acceptable to denote Li-rich material as
21 $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$. More detailed structure information of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$
22 can be seen in our previous study.¹⁶

1 Fig 2e displays the initial charge-discharge profiles of Li_2MnO_3 , $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and
2 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ at 0.1 C. For Li_2MnO_3 , only a voltage plateau above 4.4 V is
3 observed during charge.¹⁰ Instead of a very stable plateau at ~4.5 V, the inclined plateau is
4 attributed to the low conductivity of pure Li_2MnO_3 .^{10,28} During discharge, the voltage
5 declines rapidly, showing a capacity of only 126.8 mAh g⁻¹. The irreversible capacity ratio
6 (ICR), defined as irreversible capacity divided by charge capacity, was 48.85%. During
7 charge, $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ has a voltage plateau above 3.7 V, corresponding to $\text{Ni}^{2+}/\text{Ni}^{4+}$
8 and $\text{Co}^{3+}/\text{Co}^{4+}$ redox couples. It has a discharge capacity of 178.7 mAh g⁻¹ and an 18.92%
9 ICR. $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ has a capacity of 120 mAh g⁻¹ during the initial charge process,
10 which is associated with the $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{3.6+}$ redox couples.^{9,17} The plateau above
11 4.4 V corresponding to Li_2MnO_3 activation is observed and provides an additional capacity of
12 200 mAh g⁻¹. Upon discharging, $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ exhibits a sloping voltage curve
13 and has a capacity of 244.7 mAh g⁻¹ with 22.56% ICR. The discharge capacity of
14 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ is much higher than the average of Li_2MnO_3 and
15 $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$, indicating a synergistic effect between Li_2MnO_3 and the layered
16 structure in Li-rich oxide material. Lim et al. has proved that layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$
17 benefits from the structural stability of Li_2MnO_3 .¹⁸ However, the explanation for why extra
18 capacity results from the introduction of Li_2MnO_3 into layered $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ is unclear.

19 The CV profiles (for the first cycle) of Li_2MnO_3 , $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and
20 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ are shown in Fig 2f. For Li_2MnO_3 , no anodic peak emerges until ~
21 4.4 V. The current peak between 4.4 and 4.8 V is attributed to Li_2MnO_3 activation and
22 simultaneous lithium extraction. A small reductive current peak can be observed below 3.6 V

1 corresponding to $\text{Mn}^{4+}/\text{Mn}^{3+}$ reduction. The anodic and cathodic current densities of Li_2MnO_3
2 are distinctly smaller than those of $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. For
3 $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$, the first peak between 3.65 V and 4.3 V during charge corresponds to
4 $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{3.6+}$ redox couples. The second smaller peak at ~ 4.5 V is due to the
5 $\text{Co}^{3.6+}/\text{Co}^{4+}$ redox couple.¹⁷ A reduction peak centered at ~ 3.7 V is observed, which is
6 attributed to $\text{Ni}^{4+}/\text{Ni}^{2+}$ and $\text{Co}^{4+}/\text{Co}^{3+}$ redox couples. Below 3.0 V, no peak is observed, which
7 indicates no Mn^{3+} formation. The CV profile of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ shows anodic peaks
8 between 3.65 V and 4.4 V for the $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{3.6+}$ redox couples.¹⁷ The subsequent
9 oxidation peak from 4.4 to 4.8 V is due to Li_2MnO_3 activation and lithium extraction, which
10 is similar to that of Li_2MnO_3 . During reduction, the $\text{Ni}^{4+}/\text{Ni}^{2+}$ and $\text{Co}^{4+}/\text{Co}^{3+}$ redox peaks at
11 ~ 3.8 V resembles $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$.⁵

12

13 **3.2 First-cycle interfacial properties**

14 Fig 3a displays the first cycle CV curve and the simultaneous EQCM response of
15 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. The corresponding $\Delta f - \Delta Q$ (charge) plots are shown in Fig 3b and c.
16 To help interpret these observations, analogous data pure $\text{LiPF}_6/\text{EC}+\text{DMC}$, without loaded
17 materials are depicted in Fig S3.

18 The diagrams of ΔR versus E (electrode potential) of pure $\text{LiPF}_6/\text{EC}+\text{DMC}$ electrolyte,
19 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$, $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and Li_2MnO_3 during first CV cycle are shown
20 in Fig S4.

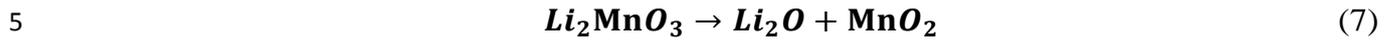
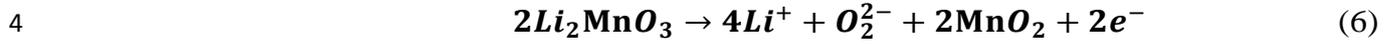
21 In many regions, the variation of ΔR is negligible (~ 0), so the Sauerbrey equation is still
22 valid, which is similar to Tsai's and Wu's reports.^{14,20} For example, in the 4.4-4.65 V region

1 during the first anodic scanning of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$, Li_2MnO_3 activation occurs and
2 the variation of ΔR is near to zero. In many other regions, the variation of ΔR is not so
3 obvious, so the mass loss/gain is the main process affecting the shift in frequency (Δf). In
4 this study, we first calculated the mass changes and mpe values by the Sauerbrey equation,
5 and then we analyzed and adjusted the mpe values with ΔR . The obtained values of these
6 parameters are listed in Table 1.

7 Fig 2e and Fig 3a illustrate that the capacity, current and Δf are all very small between
8 open circuit potential (OCP) and 3.7 V during the first charge. Changes in this region are
9 attributed mainly to absorption/desorption of electrolyte molecules or ions.²⁷ In the first
10 charge, ΔR is almost zero when the potential is below 4.65 V, which suggests the Sauerbrey
11 equation is valid in this region. It is observed that the measured mpe is close to 7 g mol^{-1}
12 (which is the atomic weight of Li) in the 4.2-4.4 V region, which indicates delithiation of Li^+
13 along with $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{3.6+}$ oxidation reactions.¹⁹ However, the mpe values in
14 3.7-4.2 V and 4.4-4.65 V are higher than 7 g mol^{-1} , indicating additional processes. For
15 analyzing the formation/dissolution of CEI, $\Delta R_{\text{CEI}}-E$ plots at different potential during the
16 first charge are displayed as a red line in Fig 3d. The corresponding Nyquist plots are shown
17 in Fig S5a-d. The equivalent circuit, shown as an insert in Fig3d, was applied to analyze the
18 EIS data. In this equivalent circuit, R_s represents the internal resistance of the battery, R_{CEI}
19 and C_{CEI} represent the resistance and capacitance of the CEI film, while R_{ct} and C_{dl} represent
20 the charge-transfer resistance and double-layer capacitance. W is the Warburg impedance
21 related to Li^+ diffusion.²¹ The fitted impedance parameters are listed in Table S1. There is
22 always native surface film on most cathode surfaces (Li_2CO_3 on lithium transition metal

1 oxides).²² This is the source of R_{CEI} in the initial state. It can be seen that the R_{CEI} decreases
2 with the potential increases in 3.7-4.2 V region, which indicates the dissolution of CEI layer.
3 There is always HF in electrolyte. Native Li_2CO_3 can react with HF and lead to dissolution.²⁴
4 Electrochemical decomposition of Li_2CO_3 was also reported by previous study.²⁷ So the
5 Li_2CO_3 degradation is a possible pathway of CEI dissolution, which can make the measured
6 *mpe* value higher. This is consistent with the high *mpe* value in 3.7-4.2 V region. In the
7 4.4-4.65 V region, R_{CEI} increases slightly, indicating new CEI film produced. So the mass
8 change is attributed to the irreversible decomposition of the Li_2MnO_3 component in
9 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and to CEI formation. Fig S3 further confirms the above analysis.
10 The decreased Δf during charge indicates no gold base dissolution (increased Δf), which
11 means gold is stable in $\text{LiPF}_6/\text{EC}+\text{DMC}$ electrolyte. The Δf vary is originated from
12 electrolyte reactions. For pure $\text{LiPF}_6/\text{EC}+\text{DMC}$ electrolyte, the absorption/desorption process
13 of electrolyte molecules/ions occurs in the OCP-4 V region. In the 4-4.65 V region, it can be
14 observed from CV curve that electrolyte begins to oxidize. Frequency decrease and negligible
15 ΔR can also be seen, corresponding to a mass increase and indicating the CEI layer derived
16 from electrolyte formed. CEI formation can reduce the calculated *mpe* value. In 3.7-4.2 V
17 region of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$, native CEI layer dissolved. But the *mpe* value in the 4-4.2
18 V region is smaller than that in 3.7-4 V, which is attributed to new CEI film formation
19 derived from electrolyte. Between 4.2 and 4.4 V, the *mpe* value is slightly smaller than 7 g
20 mol^{-1} , which is also attributed to new CEI formation. In the 4.4 V-4.65 V region, the mass
21 change is attributed to the irreversible decomposition of Li_2MnO_3 component in
22 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and to CEI formation.

1 There have been many studies about the decomposition of Li_2MnO_3 , and O_2^{2-} (true
2 species or localized electron holes on oxygen). Li_2O were proved to be formed in different
3 research.⁶⁻¹⁰ The specific reactions may follow as eq 6 and eq 7.



6 For eq 6, two electrons are transferred and four Li^+ ions are extracted. The *mpe* value of eq 6
7 is $28/2 = 14 \text{ g mol}^{-1}$ and Li^+ extraction can lead to mass loss. For eq 7, no electrons are
8 transferred and no species are lost from the material, so the mass change of eq 7 is zero. As
9 can be seen in Table 4, the maximum of mass loss of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ in 4.4-4.65 V
10 region is 277.4 ng when eq 6 is the only reaction. However, the real mass loss is 137.5 ng,
11 which is 49.57% of the maximal mass loss originating from Li_2MnO_3 activation. Considering
12 that CEI film formation leads to mass gain, and chemical decomposition according to eq 7
13 does not affect the mass, electrochemical decomposition according to eq 6 is the main process
14 of Li_2MnO_3 activation for Li-rich oxide $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. The measured *mpe* value in
15 4.4-4.65 V region is 12.85 g mol^{-1} , which is slightly smaller than 14 for eq 6. CEI film
16 formation leads to a mass gain for the electrode, but no electrons transfer of electrode
17 material, and makes the measured *mpe* value smaller, which is consistent with our experiment.
18 In the region above 4.65 V, the ΔR is slightly increased, and a further oxidation reaction of
19 electrolyte occurs because of the high charge voltage.

20 Fig 3c illustrates the $\Delta f - \Delta Q$ plot during the first discharge process, and the
21 corresponding mass change and *mpe* values are listed in Table 1. ΔR increases during the
22 first discharge, which leads to a negative shift of frequency. So the actual shift of frequency

1 caused by the mass gain is smaller than that observed in Fig 2c, and the real *mpe* value is
2 smaller than that listed in Table 1. In the 4.8-4.1 V region, a continuous oxidation reaction of
3 electrolyte occurs. In the region below 2.6 V, a decomposition reaction of electrolyte occurs,
4 which is consistent with the very small capacity in the charge-discharge curve, as
5 demonstrated in Fig 2e. Considering the previous reports and our experimental data (*mpe* =
6 53.42, ΔR increase), Li_2CO_3 (*mpe* =37) is one of the possible product.^{10,28} In these two
7 regions, there are no valence state changes for the metal ions in $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$, and
8 the interfacial reactions for $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and pure electrolyte are very similar. In
9 the 4.1-2.6 V region, the insertion of Li^+ causes the mass to increase. However, the *mpe* value
10 in the 4.1-2.6 V region is higher than 7 g mol^{-1} , indicating that the insertion of Li^+ maybe not
11 be the only electrochemical process. But considering the shift of frequency caused by ΔR ,
12 more proof should be given. The blue line in Fig 3d displays the $\Delta R_{\text{CEI-E}}$ plot of
13 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ at different potentials during the first discharge. The corresponding
14 Nyquist plots are shown in Fig S5e-f, and the fitted impedance parameters are listed in Table
15 S2. It is observed that R_{CEI} increases as the potential decreases in the 4.1-2.6 V region.
16 Considering that the *mpe* value is greater than 7 g mol^{-1} , a new CEI film with lower
17 conductivity has apparently formed in this region. For pure $\text{LiPF}_6/\text{EC}+\text{DMC}$ electrolyte, the
18 frequency change is slightly higher in the 4.1-2.6 V region. Considering that an increase in
19 ΔR leads to negative shift of frequency, the measured frequency increase implies CEI
20 dissolution and mass loss. The difference between pure electrolyte and
21 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ is attributed to the valence state changes of metal ions in this region,

1 since the interfacial reactions are very similar when there are no valence state changes of
2 metal ions in the region above 4.1 V and below 2.6 V.

3 To further clarify the interfacial property of Li-rich $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ material,
4 the interfacial properties of layered $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and pure Li_2MnO_3 were also
5 investigated for comparison. As demonstrated in Fig 4a, the CV curve during the first cycle
6 and the simultaneous EQCM response of $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ can be observed. The
7 corresponding $\Delta f-\Delta Q$ plots are shown in Fig 4c and 4e. Table 2 summarizes the mass change
8 and *mpe* values during first cycle. As with $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$, electrolyte
9 absorption/desorption occurs below 3.65 V. The *mpe* value in the 3.65-3.9 V region is near 7
10 g mol^{-1} and ΔR is insignificant, which indicates delithiation along with $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/$
11 $\text{Co}^{3.6+}$ oxidation. In the 3.9-4.4 V region, ΔR increases slightly, while the *mpe* value varies.
12 The large *mpe* values indicate that dissolution of the native CEI layer is the dominated
13 process, as with $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. When the potential is above 4.4 V, the variation of
14 ΔR is near to zero and the Sauerbrey equation is applicable. In the 4.4-4.53 V region, $\text{Co}^{3.6+}/$
15 Co^{4+} oxidation reactions occur along delithiation.¹⁷ The *mpe* value in the 4.4-4.53 V region is
16 6.73 g mol^{-1} , which is slightly smaller than 7 g mol^{-1} . This result demonstrates that Li^+
17 extraction along with $\text{Co}^{3.6+}/\text{Co}^{4+}$ oxidation are the main processes in this region. Nyquist
18 plots of $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ shown in Fig S6 also illustrate that R_{CEI} is slightly increased,
19 indicating that there is new CEI film formed. When the voltage is higher than 4.65 V,
20 electrolyte oxidation occurs. For the first discharge of $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$, it is very similar
21 to that of Li-rich $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. ΔR increases during first discharge, as with
22 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. Continuous electrolyte oxidation occurs in the 4.8-4.1 V region and

1 electrolyte is decomposed when the potential is below 2.6 V. Between 4.1 and 2.6 V, Li⁺
2 insertion is accompanied by metal ion reduction and CEI film formation.

3 Fig 4b shows the CV curve for the first cycle and the simultaneous EQCM response of
4 Li₂MnO₃. The corresponding $\Delta f - \Delta Q$ (charge) plots are displayed in Fig 4d and f. Table 3
5 summarizes the *mpe* value during first cycle. For the Li₂MnO₃ electrode, ΔR increases when
6 the voltage is below 3.8 V but hardly varies when the potential is above 3.8 V. There is no
7 obvious electrochemical reaction besides the absorption/desorption of electrolyte
8 molecule/ion when the potential is below 3.8 V. In the 3.8-4.05 V region, the native CEI film
9 dissolves, as with the case of Li-rich material. In the region between 4.05 and 4.4 V, new CEI
10 is produced. In the 4.4-4.65 V region, the Sauerbrey equation is valid and the decomposition
11 of Li₂MnO₃ is the dominant reaction. As displayed in Table 4, the mass of loaded Li₂MnO₃ is
12 4.777 μg . The maximum extracted Li⁺ is 567.589 ng when eq 6 is the only decomposition
13 pathway. However, the real mass loss of Li₂MnO₃ is only 7.959 ng, only 1.4% of the
14 maximal mass loss from Li₂MnO₃ activation and much smaller than 49.57% of Li-rich oxide.
15 The *mpe* value is 1.51 g mol⁻¹, which is distinctly smaller than the 14 g mol⁻¹ of eq 6. This
16 result indicates that CEI film formed. Considering that the new CEI film formation can
17 counter some of the mass loss, we conclude that a chemical decomposition of Li₂MnO₃ to
18 Li₂O and MnO₂ is the dominant reaction, as shown in eq 7, which coincides with the
19 electrochemical results in Fig 2f.

20 However, electrochemical decomposition is the main process of Li₂MnO₃ component in
21 Li-rich oxide Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O₂. The obviously different routes of Li₂MnO₃
22 decomposition reactions in the same potential region demonstrates that there is a synergistic
23 effect between Li₂MnO₃ (*C2/m*) and the layered structure (*R $\bar{3}m$*) in Li-rich oxide material,

1 which is in accordance with the first charge-discharge profiles in Fig 2e. Pure chemical
2 decomposition does not contribute to capacity. So the different decomposition pathway of
3 Li_2MnO_3 in Li-rich oxides is the reason why Li-rich oxides can provide higher capacity than
4 pure Li_2MnO_3 and $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ materials.

5 The first discharge of pure Li_2MnO_3 is also very similar to that of Li-rich oxide, where
6 electrolyte oxidation occurs in the 4.8-3.9 V region and electrolyte is decomposed for
7 potentials below 2.6 V. In the region between 3.9 and 2.6 V, Li^+ inserts into the electrode and
8 CEI is formed. But there is some difference. The *mpe* value is much smaller than that of
9 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$, indicating that changes in the valence state
10 of Ni^{4+} and Co^{4+} have a bigger effect on CEI formation than those of Mn^{4+} and O_2^{2-} .

11 Scheme 1a demonstrates the EQCM working principle in this work. The Li^+
12 insertion/extraction and SEI evolution occurring on the electrodes lead to mass change, which
13 can be measured by the frequency change of crystal quartz. The CV curves can also be
14 recorded, which can be used to calculate the charge evolution during the test. Combining the
15 mass change and charge evolution, we can get the *mpe* value, which is closely related with
16 different kinds of reactions and important to determine what reactions occur in different
17 potential region, such as Li_2MnO_3 activation in 4.4-4.65 V region during first charge. Scheme
18 1b illustrates the proposed interfacial reaction mechanism of Li-rich oxides during the first
19 charge, based on the previous results in this article. Solvated electrolyte ions adsorb on the
20 surface of the electrode in the initial period. Subsequently, Li^+ extracts from material. When
21 the potential is below 4.4 V, Ni^{2+} is oxidized to Ni^{4+} to compensate for the Li^+ extraction.
22 Native CEI dissolution takes place at the same time. In the voltage region between 4.4 V and
23 4.65 V, Li_2MnO_3 activation and new CEI formation occurs. At higher potentials, electrolyte
24 oxidation is the dominant reaction. Detailed reactions in the Li_2MnO_3 activation region of
25 Li-rich oxides and pure Li_2MnO_3 are depicted in scheme 1c. For pure Li_2MnO_3 , the activation

1 process is mainly chemical decomposition to Li_2O and MnO_2 . However, for Li-rich oxides,
2 electrochemical decomposition to Li^+ , O_2^{2-} and MnO_2 is the dominant pathway. The proposed
3 main interfacial reaction mechanism of Li-rich oxides during first discharge is illustrated in
4 Scheme 1d. Continuous electrolyte oxidation occurs in the high voltage. After the voltage
5 dropping to 4 V, Li^+ insertion accompanied by metal ion and O_2^{2-} reduction subsequently
6 occurs, while CEI forms in the same time. When the voltage is below 2.6 V, electrolyte
7 decomposition is the main process.

8

9 **4. Conclusions**

10 In summary, we investigated the Li_2MnO_3 activation pathway and CEI formation/dissolution of
11 $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ ($x = 0, 0.5, 1$) cathode materials in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}$ by
12 in-situ EQCM and EIS. A synergistic effect between layered Li_2MnO_3 and $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$
13 component that explains the extra-high capacity for $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ cathode was found. The
14 synergistic effect in Li-rich $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ cathodes can affect the activation pathway of
15 the Li_2MnO_3 component in Li-rich material. Specifically, the activation of pure Li_2MnO_3 is governed
16 by chemical decomposition to Li_2O . However, Li_2MnO_3 activation in Li-rich material is dominated
17 by electrochemical activation to O_2^{2-} (oxygen redox). Chemical decomposition does not contribute
18 to the electrode capacity because there is no delithiation. This explains why Li-rich materials
19 ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$) have a higher capacity than the mean value of Li_2MnO_3 and
20 $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$.

21 Besides activation of Li-rich materials, it has been observed that CEI formation/dissolution
22 accompanies Li^+ extraction/insertion. We also found that changes in the valence state of metal ions
23 (Ni, Co, Mn) in Li-rich material can promote CEI formation. Focusing on reducing chemical

1 decomposition during first-cycle activation, and controlling the promotion of metal ions valence
2 states changes should provide a route to improve the electrochemical performance of Li-rich
3 materials.

5 **ASSOCIATED CONTENT**

6 **Supporting Information**

7 Impedance parameters of Li-rich $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ at different potentials during first cycle;
8 Optical micrograph of Li-rich material coated EQCM electrode; Refinement XRD patterns of Li-rich
9 material; CV-EQCM test data of pure $\text{LiPF}_6/\text{EC}+\text{DMC}$ electrolyte without loaded materials;
10 Evolution of resistance (ΔR) of pure electrolyte, Li-rich, layered oxide and Li_2MnO_3 during first
11 cycle; EIS results of Li-rich $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ at different potentials during first cycle; EIS
12 results of layered $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ during first charge.

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18 **Notes:**

19 The authors declare no competing financial interest.

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4

1 **Table and figure captions:**

2

3 **Table 1.** The mass change and mpe values measured from the EQCM data for
4 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ during first cycle. The frequency change of pure $\text{LiPF}_6/\text{EC}+\text{DMC}$
5 (LP) electrolyte was given as comparison. The mass of loaded $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$
6 material is 4.258 μg .

7 **Table 2.** The mass change and mpe values measured from the EQCM data for
8 $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ during first charge. The mass of loaded $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ material is
9 4.209 μg .

10 **Table 3.** The mass change and mpe values measured from the EQCM Data for Li_2MnO_3
11 during first charge. The mass of loaded Li_2MnO_3 material is 4.777 μg .

12 **Table 4.** Comparison of mass changes of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and Li_2MnO_3 materials in
13 4.4-4.65 V region.

14 **Fig 1.** (a) Schematic diagram of EQCM setup.

15 **Fig 2.** SEM images of: (a) Li_2MnO_3 , (b) $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and (c) $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$; (d)
16 XRD patterns for the three samples; (e) Initial charge-discharge profiles at 0.1 C and (f) CV
17 curves for the first cycle of Li_2MnO_3 , $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$. The
18 scan rate of CV curves is 0.2 mV s^{-1} .

19 **Fig 3.** (a) CV curve for first cycle and the simultaneous EQCM response of
20 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$; Plots of Δf versus ΔQ for $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ (b) during
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1 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ at different potential during first charge-discharge process, and the
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5 during anodic scanning and (e) during cathodic scanning; Plots of Δf versus ΔQ for Li_2MnO_3
6 (d) during anodic scanning and (f) during cathodic scanning.

7 **Scheme 1. (a) Diagram Showing the EQCM Working Principle in this Work; (b) Proposed**
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9 **the Li_2MnO_3 Activation Voltage Region of Li-rich oxides and Pure Li_2MnO_3 ; (d) Proposed**
10 **Main Interfacial Reaction Mechanisms during First Discharge.**

11

1 **Table 1.** The mass change and mpe values measured from the EQCM data for
2 $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ during first cycle. The frequency change of pure $\text{LiPF}_6/\text{EC}+\text{DMC}$
3 (LP) electrolyte was given as comparison. The mass of loaded $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$
4 material m_1 is 4.258 μg .

	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
Δf -pure LP (Hz)	-1.91	-1.461	-1.88	-4.51	-8.02	1.26	2.42	-0.45	-6.97
Δf (Hz)	67.27	60.86	22	102.6	-6.2	29.3	-102.5	-79.65	-310.8
Δm (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^{-1})	-32.23	-19.72	-6.03	-12.85	0.42	-1.39	25.33	34.94	53.42
ΔR		~ 0			↑		↑		

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1 **Table 2.** The mass change and mpe values measured from the EQCM data for
 2 $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ during first charge. The mass of loaded $\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$ material m_2
 3 is 4.209 μg .

	Charge						Discharge				
potential region (V)	3.65	3.9-	4.1-	4.4-	4.53-	4.65	4.8-	4.1-	3.9	3-	2.6
	-3.9	4.1	4.4	4.53	4.65	-4.8	4.1	3.9	-3	2.6	-2
Δf (Hz)	42.45	134.44	132.2	44.9	19.3	21.7	6.2	-38.7	-117	-45.9	-288.7
Δm (ng)	-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^{-1})	-8.46	-56.5	-38.62	-6.73	-2.92	-1.6	-0.24	61.4	20.1	30.8	53.4
ΔR	~ 0	\uparrow	\downarrow	~ 0	\uparrow				\uparrow		

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1 **Table 3.** The mass change and mpe values measured from the EQCM Data for Li_2MnO_3
 2 during first charge. The mass of loaded Li_2MnO_3 material m_3 is $4.777 \mu\text{g}$.

	Charge						Discharge				
potential region (V)	OCP	3.8-	4.05	4.4-	4.65-	4.75	4.8-	3.9-	3.3	3-	2.6
	-3.8	4.05	-4.4	4.65	4.75	-4.8	3.9	3.3	-3	2.6	-2
Δf (Hz)	-29.34	3.06	-30.66	5.34	-13.94	-5.65	42.81	-6.79	-5.28	-4.18	-196.5
Δm (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^{-1})	58.96	-8.45	21.34	-1.51	4.31	2.37	-2.69	16.74	7.55	3.34	50.12
ΔR		↑	~0	~0		↑	~0	↓	~0	↑	~0

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1 **Table 4.** Comparison of mass changes and mpe value of $\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ and
 2 Li_2MnO_3 materials in 4.4-4.65 V region.

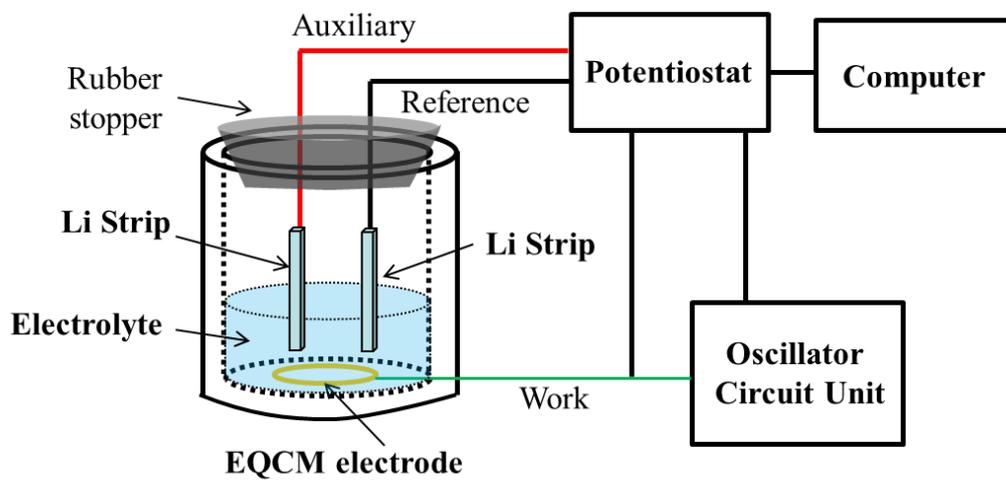
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	$\text{Li}_{1.2}\text{Ni}_{0.12}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$ ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.4}\text{O}_2$)	Li_2MnO_3
Mass of loading active material (μg)	4.258	4.777
Mass ratio of Li^+	9.774%	11.882%
The maximum of mass change of Li^+ extraction (ng)	-416.164	-567.589
The maximum of mass change of Li_2MnO_3 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

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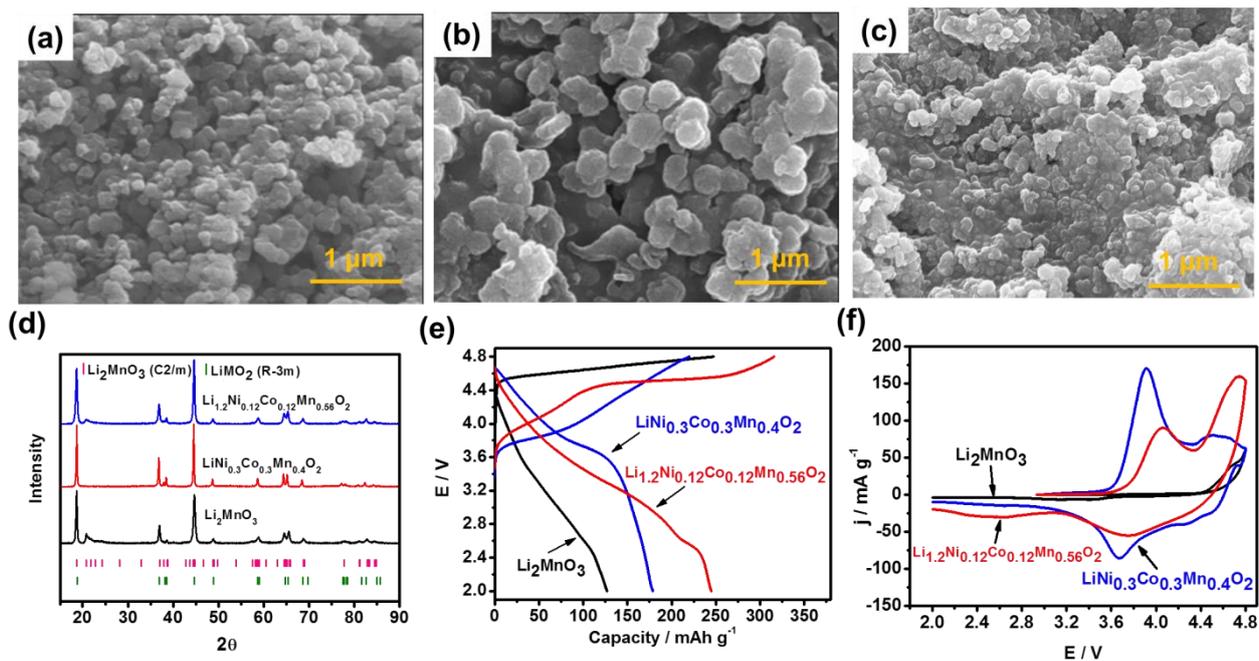
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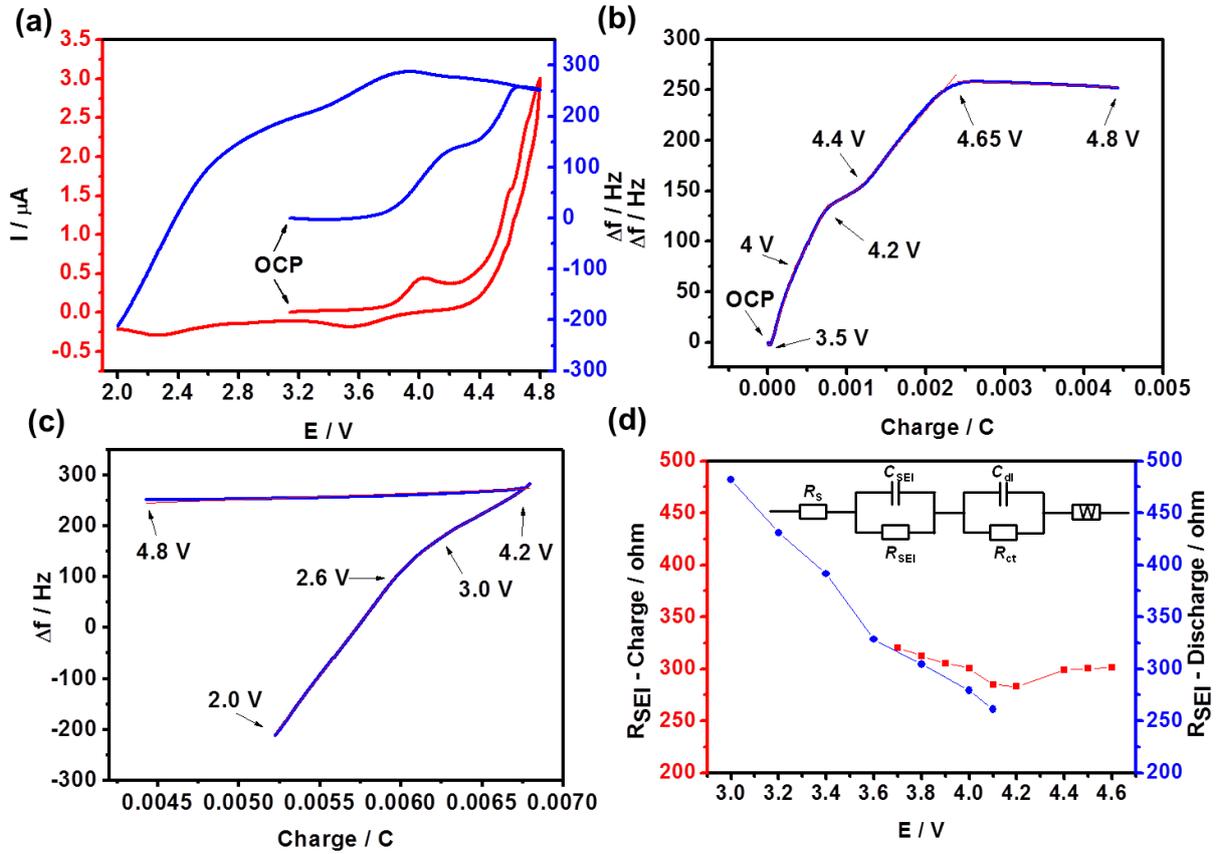
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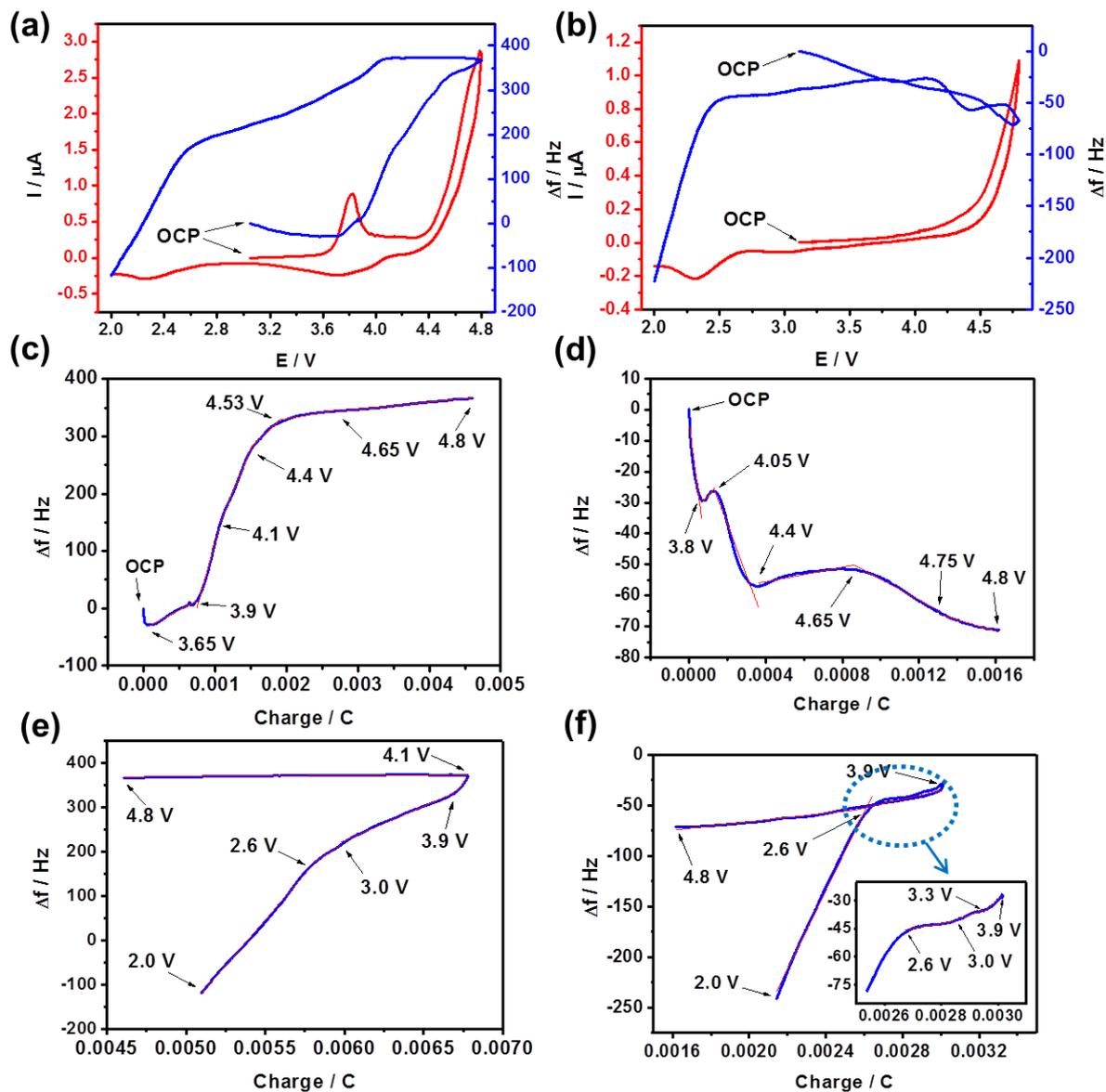
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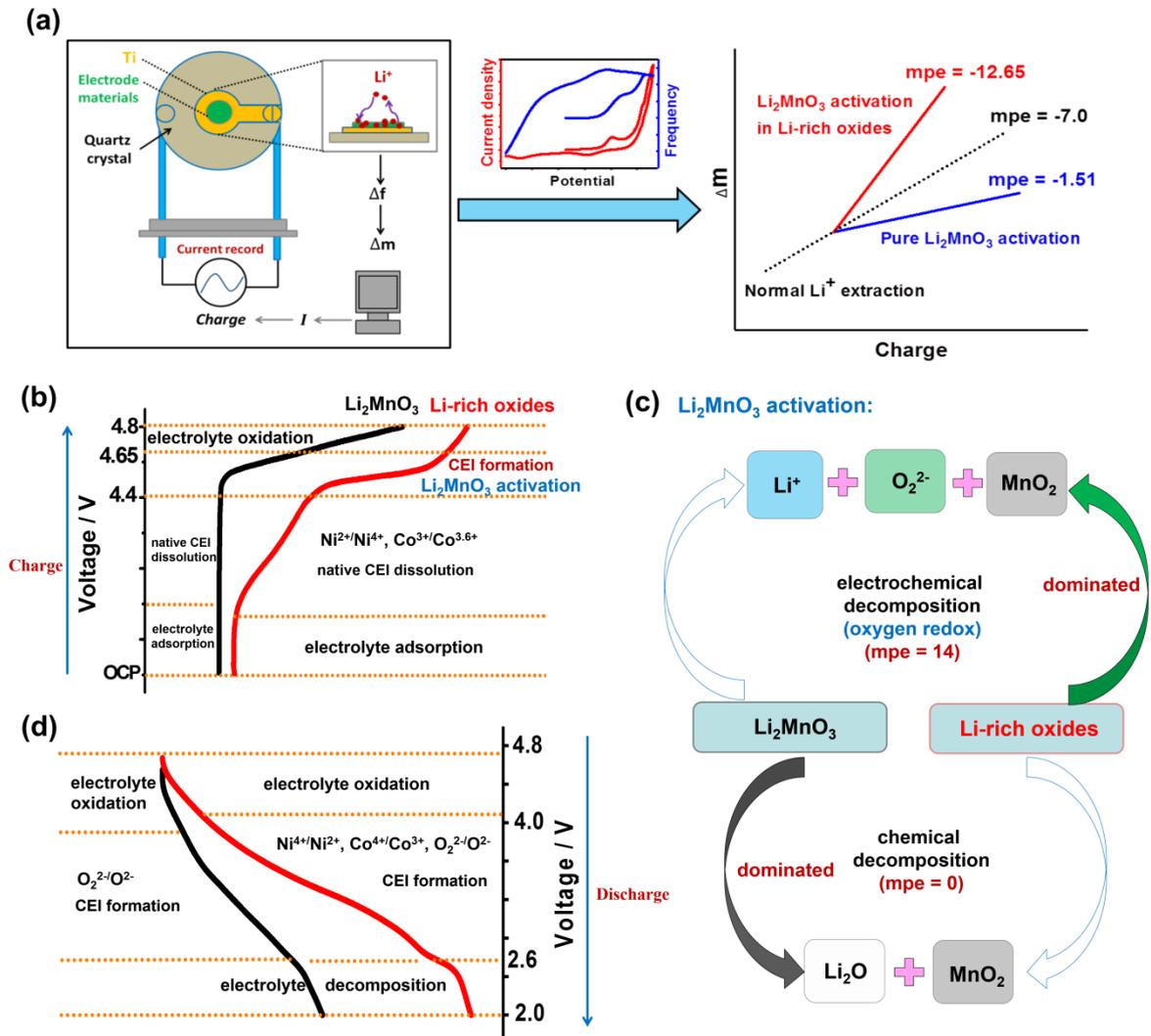
4 during anodic scanning and (e) during cathodic scanning; Plots of Δf versus ΔQ for Li_2MnO_3

5 (d) during anodic scanning and (f) during cathodic scanning.

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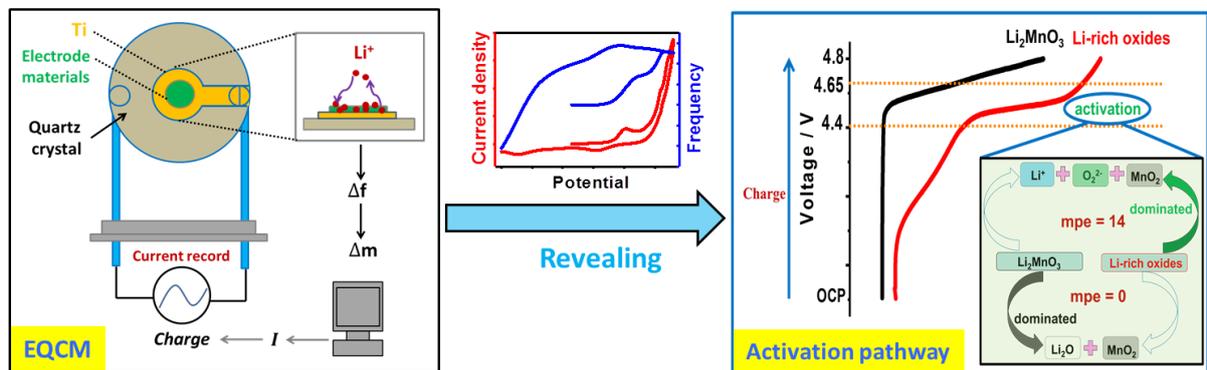


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1 **Table of content**

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