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# Dual-site Doping to Enhance Oxygen Redox and Structural Stability of Li-rich Layered Oxides

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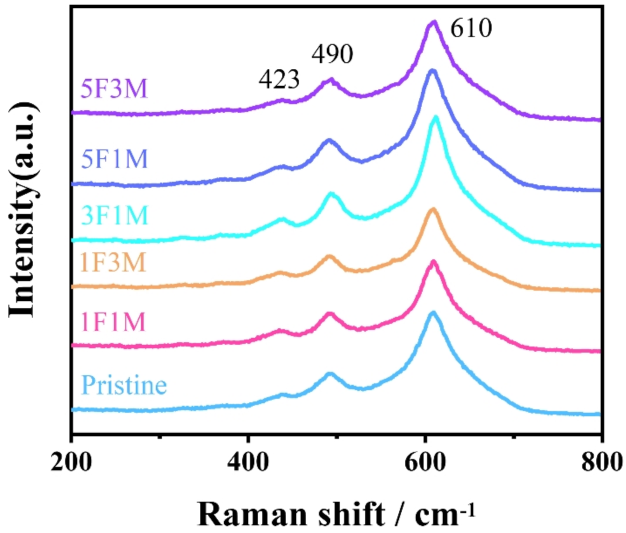


**Figure S1.** (a) Raman spectra of the Pristine and dual-site doping samples.

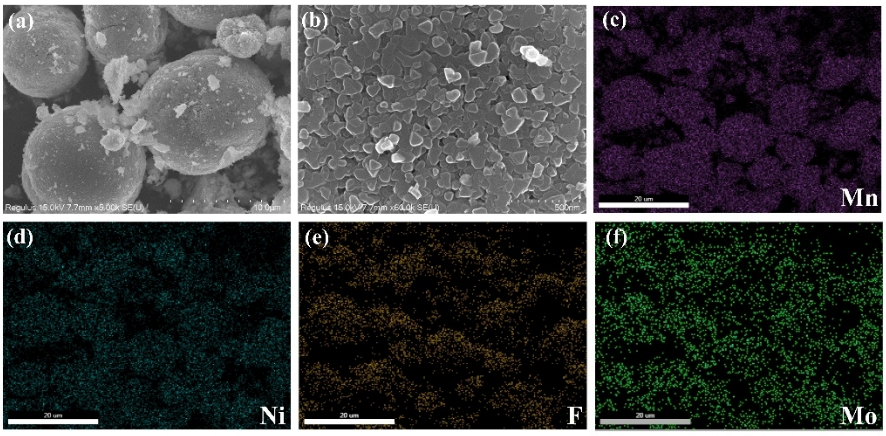


**Figure S2.** SEM images of (a-b) 1F3M material and the elemental mapping of (c) Mn, (d) Ni, (e) F, and (f) Mo.

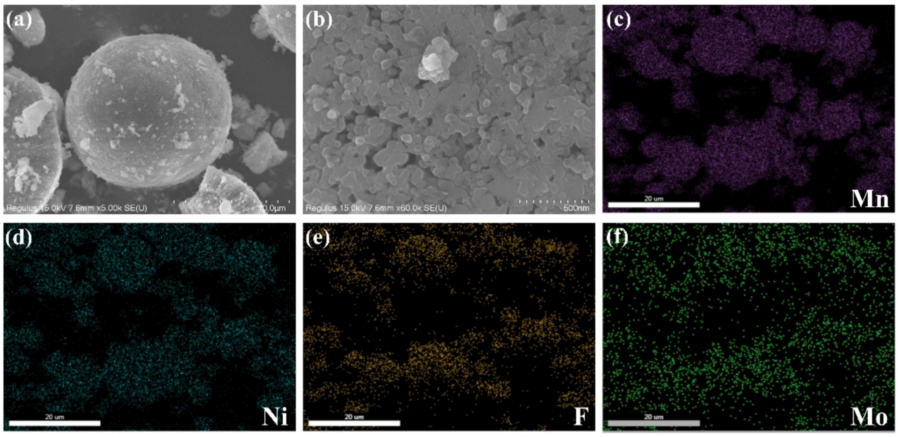


**Figure S3.** SEM images of (a-b) 5F1M material and the elemental mapping of (c) Mn, (d) Ni, (e) F, and (f) Mo.

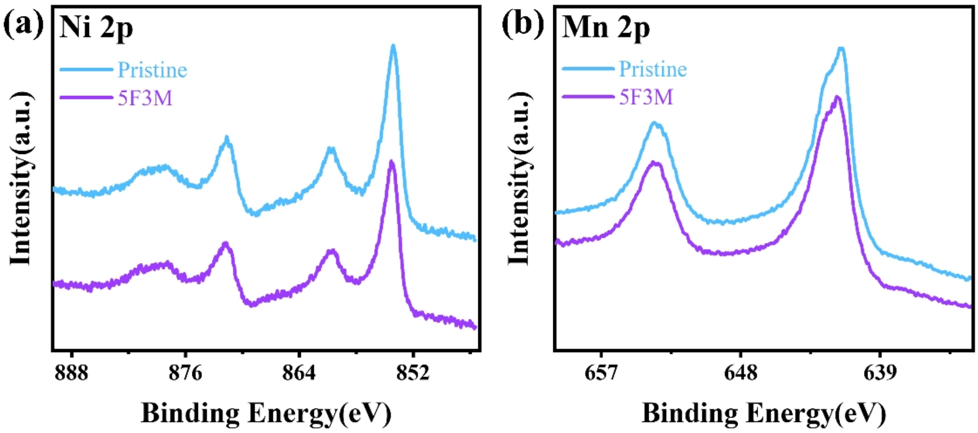


**Figure S4.** XPS spectra of (a) Ni 2p, (b) Mn 2p for Pristine and 5F3M sample.

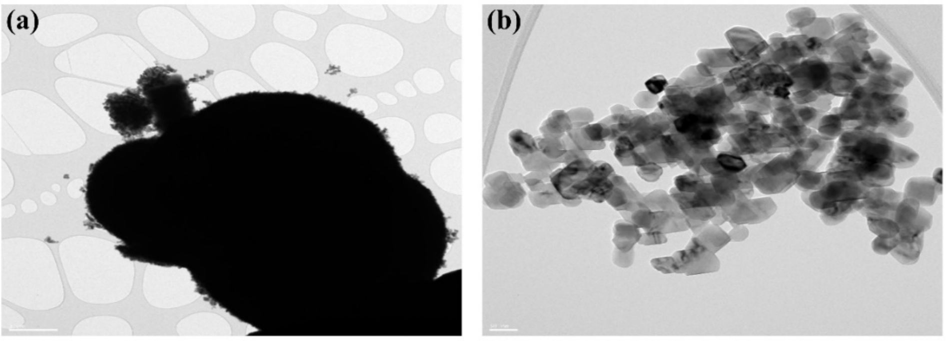


**Figure S5.** TEM image of the Pristine sample for a microsphere morphology.

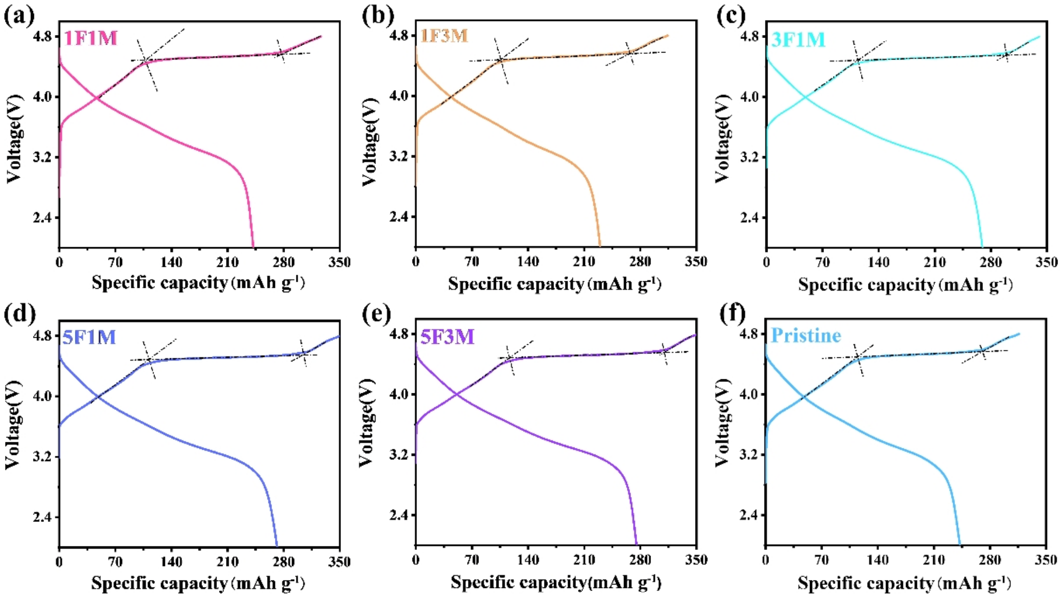


**Figure S6.** A method of obtaining the capacities provided by layered and $Li_2MnO_3$ phases.

Chinese Journal of Structural Chemistry

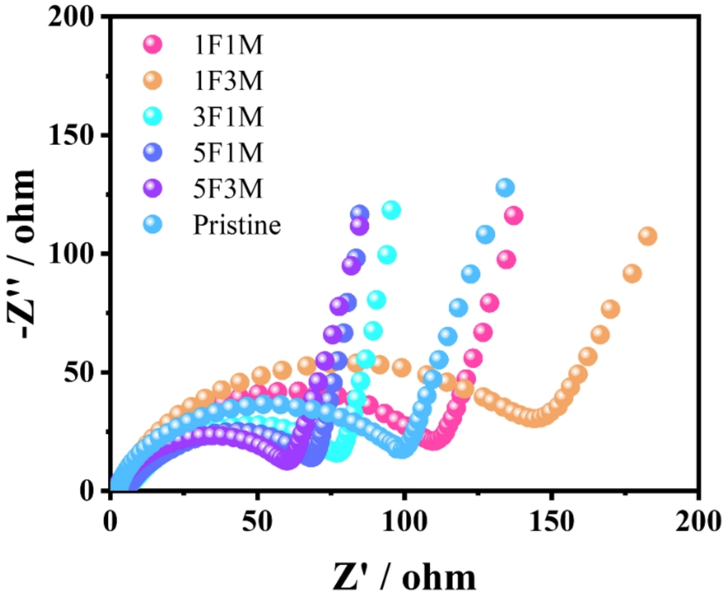


**Figure S7.** The Nyquist plots of all samples

Chinese Journal of Structural Chemistry

**Table S1.** Structure Parameters of $LiMO_2$ Used in the Refinements of the 5F3M Sample

| $R_p$ = 12.7 | | | $R_{wp}$ = 5.70 | | $\chi^2$ = 0.444 |
|---|---|---|---|---|---|
| Atom | *x* | *y* | *z* | *Occ* | Uiso |
| Li1 | 0 | 0 | 0 | 0.992(3) | 0.025 |
| Mn1 | 0 | 0 | 0.5 | 0.478(2) | 0.025 |
| Ni1 | 0 | 0 | 0.5 | 0.497(1) | 0.025 |
| Mo1 | 0 | 0 | 0.5 | 0.017(1) | 0.025 |
| O1 | 0 | 0 | 0.2415(4) | 1 | 0.025 |
| Li2 | 0 | 0 | 0.5 | 0.008(3) | 0.025 |
| Mo2 | 0 | 0 | 0 | 0.008(3) | 0.025 |

**Table S2.** Capacity Contributed by Layered and $Li_2MnO_3$ Phases during the First Charge Process

| Sample | Layered phase | $Li_2MnO_3$ phase | Total charging capacity |
|---|---|---|---|
| 1F1M | 108.7 | 167.6 | 326.1 |
| 1F3M | 106.6 | 159.6 | 314.3 |
| 3F1M | 115 | 183.8 | 340.7 |
| 5F1M | 113.1 | 189.7 | 349.4 |
| 5F3M | 117.6 | 190.9 | 351.1 |
| Pristine | 115.8 | 153.9 | 316.2 |

**Table S3.** A Comparation of Specific Capacity between This Work and Other Cobalt-free Li-rich Layered Oxides

| Modification strategy | Voltage(V) | Discharge specific capacity (mAh/g) | Discharge specific capacity after cycle (mAh/g) | References |
|---|---|---|---|---|
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by polypyrrole coated | 2.0–4.8 | 236.8(0.1C) | 202.93 (0.1C, 100 cycles) | [1] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by Fe doping | 2.0-4.8 | ~260(0.1C) 192(1C) | 164.16 (1C, 200 cycles) | [2] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by C coated | 2.0-4.8 | ~260(0.1C) 226.2(1C) | 189.7 (1C, 100 cycles) | [3] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by $TiO_2$ coated | 2.0-4.8 | 257.5(0.05C) ~181(1C) | ~176 (1C, 40 cycles) | [4] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by $Na^+$ and $Al^{3+}$ doped | 2.0-4.8 | 262.66(0.1C) 210.1(1C) | ~185.22 (1C, 200 cycles) | [5] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by $Mn_3O_4$ coated | 2.0-4.8 | 251(0.1C) 208.6(1C) | 199.5 (1C, 200 cycles) | [6] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ with exposed {010} planes | 2.0-4.8 | ~280(0.1C) ~225(1C) | ~224 (1C, 60 cycles) | [7] |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by $Li_2SnO_3$ coated | 2.0-4.8 | 255(0.1C) 190(1C) | 196.2 (1C, 200 cycles) | [8] |
| **$Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by dual-site doping** | **2.0-4.8** | **275(0.1C) 246(1C)** | **190.98 (1C, 100 cycles)** | **Our work** |

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