

## Supporting Information

Surface Heterostructure Induced by  $\text{PrPO}_4$ -modifying in  $\text{Li}_{1.2}[\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  cathode material for high performance lithium ion batteries with Mitigating Voltage Decay

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## Experimental details

**Synthesis of Bare and PrPO<sub>4</sub> modified Li-Rich Samples:** Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> powder was synthesized by a hydroxide co-precipitation method followed by high temperature calcination as described in a previous report.<sup>1</sup> Nickel sulfate hexahydrate (NiSO<sub>4</sub>·6H<sub>2</sub>O), manganese sulfate monohydrate (MnSO<sub>4</sub>·H<sub>2</sub>O), cobalt sulfate heptahydrate (CoSO<sub>4</sub>·7H<sub>2</sub>O), potassium hydroxide (KOH), and ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O) were used as the starting materials to prepare the Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>(OH)<sub>1.6</sub> precursor. The precursor material was thoroughly washed several times by filtering with deionized water to remove residual potassium and sulfate species, then dried in a vacuum oven at 120°C overnight. The dried powder was mixed with stoichiometric LiOH·H<sub>2</sub>O (5wt% excess) and preheated at 450°C for 5 h before calcinated at 900°C for 18h in the air, and then cooled to room temperature in the indoor environment to obtain the final product.

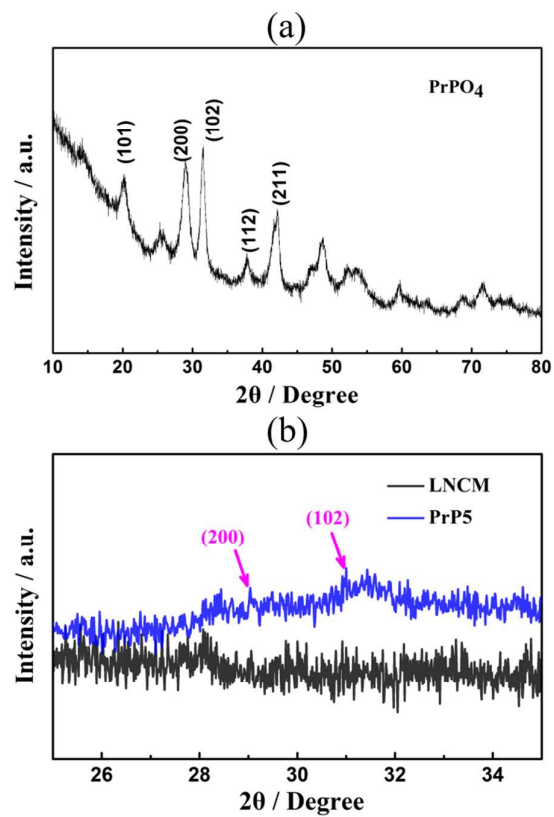
PrPO<sub>4</sub> modified Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> particles are synthesized using a PVP-assisted wet chemical deposition method. Certain amounts of Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were first dissolved in X mL deionized water and 20mL ethylalcohol mixed solution, in which 0.5g of polyvinyl pyrrolidone (PVP) and 1g Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> powders had been previously dissolved and dispersed at 50°C for 2h. And then 0.02M ammonium dihydrogen phosphate solution (0.02M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) was added dropwise and stirred at room temperature for more than ten minutes, in which process the total amount of deionized water in the suspension was just the same as ethylalcohol for promising the same reaction condition. After stirred for 3 h, the resulting mixture was heated to 75°C and stirred vigorously until the solution was evaporated to dryness. Finally, the obtained powder was calcined at 450 °C in a muffle furnace for 5 h, and then cooled to room temperature to get the PrPO<sub>4</sub> modified Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> material. The samples with different PrPO<sub>4</sub> coating amounts of 2, 3, and 5 wt % are labeled as PrP2, PrP3, and PrP5, respectively, besides the pristine powders were also prepared through the same process to exclude the influence of the coating process, labelled as LNCM. The pure PrPO<sub>4</sub> sample was also prepared by the wet chemical deposition method under the same conditions.

**Materials Characterizations:** The crystal structures of all the samples were

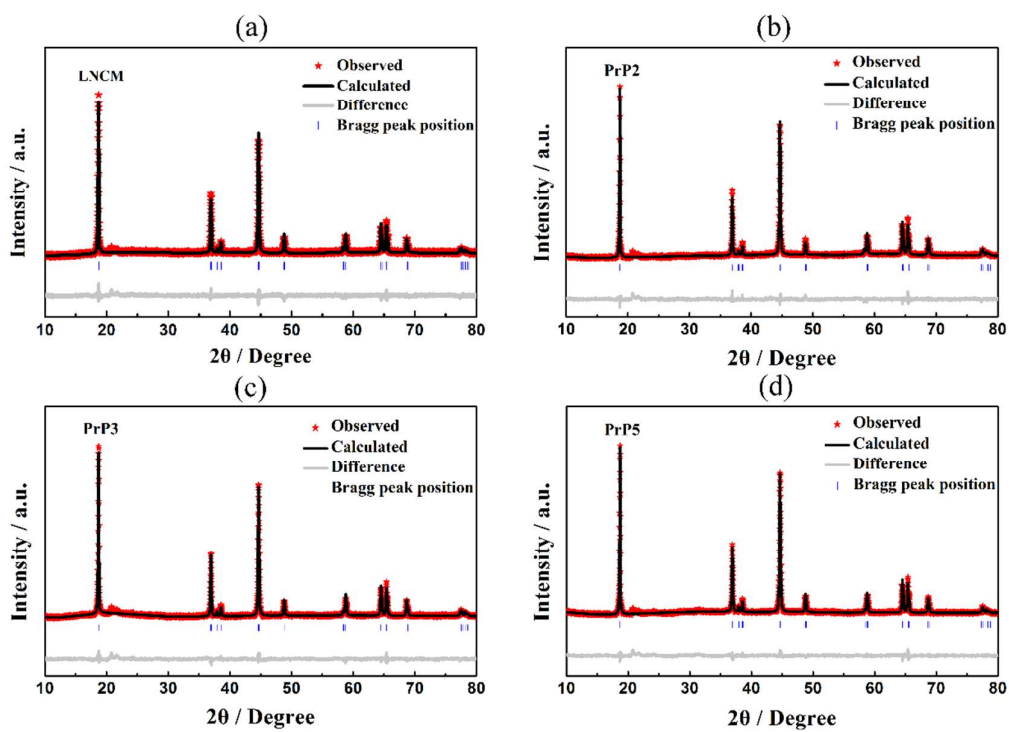
characterized using X-ray diffraction (XRD; PANalytical, PW 3040-X'Pert Pro) with step size of  $0.013^\circ$  and a speed of  $2^\circ \text{ min}^{-1}$  over a  $2\theta$  range of  $10\text{--}80^\circ$ , operating at 40 kV and 40 mA with a Cu  $K\alpha_{1/2}$  radiation source. Morphological studies on the samples were performed using a field emission scanning electron microscope (FESEM, Zeiss SUPRATM55) with an accelerating voltage of 15 kV and transmission electron microscopy (TEM, JEM- 2010F). More detailed surface structure and the elements distribution were investigated by high resolution transmission electron microscopy (HRTEM , JEM- 2010F) equipped with energy-dispersive X-ray spectroscopy (EDS). The XPS measurement was performed on a PHI Quantera II SXM system (Japan/Ulvac-PHI, Inc.), using a monochromatized Al  $K\alpha$  radiation source. Binding energies were calibrated using the containment carbon (C 1s = 284.6 eV), and the O 1s and Pr 3d spectra were fitted using a Gaussian line profile by CASAXPS software. Raman spectroscopic measurement was conducted on primary pristine and PrP3 samples at room temperature, using a Raman microscope (LabRAM HR Evolution, HORIBA), equipped with a solid state laser with a wavelength of 532 nm.

**Electrochemical measurements:** The electrodes were fabricated from 75 wt.% active materials, 15 wt.% carbon black (Super-P), and 10 wt.% polypropylene difluoride (PVDF). Active material and Super-P were first mixed thoroughly, then PVDF binder dissolved in N-methyl pyrrolidone (NMP) solvent was added. The slurry was uniformly coated on an aluminum foil and dried at  $120^\circ\text{C}$  overnight. The electrodes were punched into round disks of 16 mm in diameter with an active material loading amount of 4-5 mg. Standard 2032 coin cells were assembled in an Ar-filled glove box, consisted of an as-prepared cathode, a Li metal anode, a Celgard 2400 separator and 1 M  $\text{LiPF}_6$  in EC-DMC (weight ratio 1:1) electrolyte solution. Galvanostatic charge and discharge tests were performed between 2.0 and 4.8 V (vs.  $\text{Li}^+/\text{Li}$ ) with a LAND CT-2001A instrument (Wuhan, China) at room temperature (around  $15^\circ\text{C}$ ). The electrochemical impedance spectroscopy (EIS) of the coin cells were recorded by VMP2 electrochemical station (Princeton Applied Research VersaSTAT3) in the charged state of 4.0 V at room temperature between 1 MHz and 10 mHz with an AC voltage of 5mV.

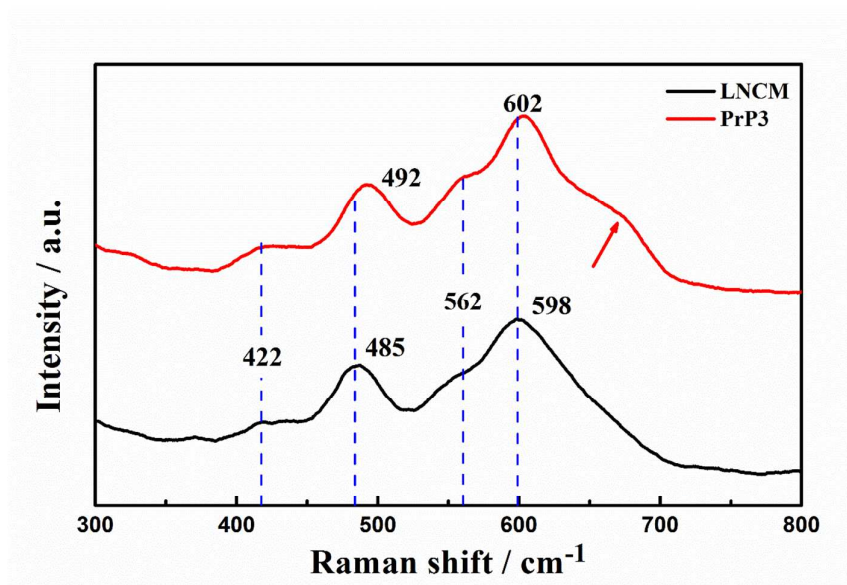




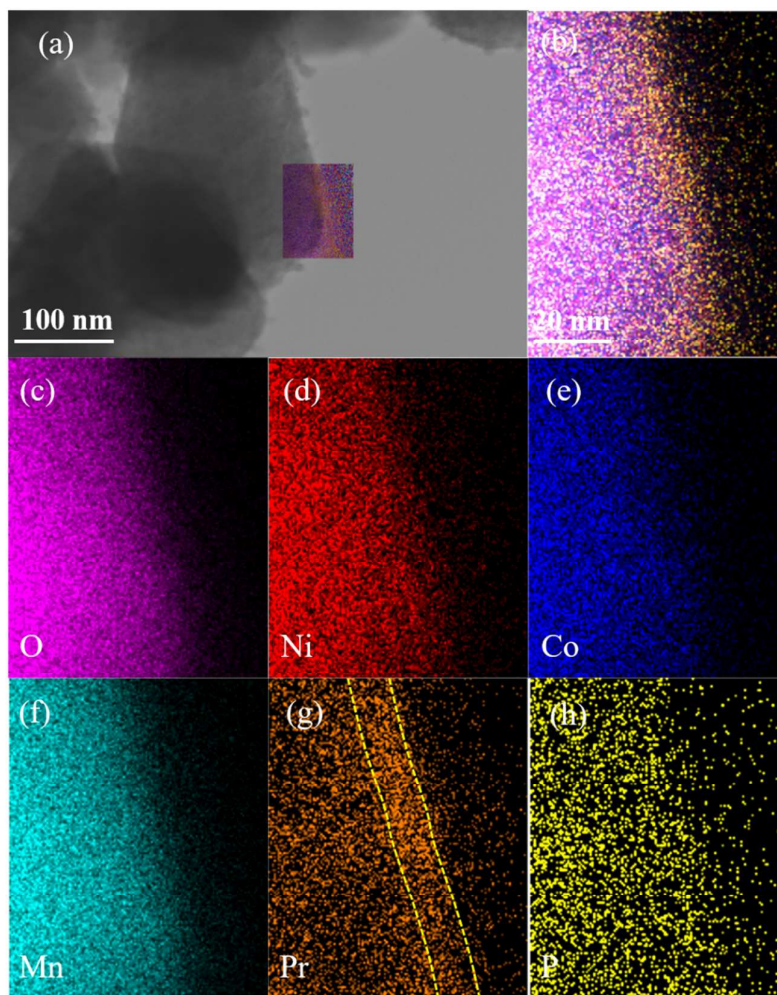
**Fig S1.** In order to identify the crystalline structure of modifying layer, (a) XRD data of pure PrPO<sub>4</sub> was collected; (b) The partial enlarged detail of XRD patterns of the LNCM and PrP5



**Fig S2.** Reitveld fitting of the XRD patterns of (a) as-prepared LNCM, (b) PrP2, (c) PrP3 and (d) PrP5 based on the hexagonal R-3m space group.

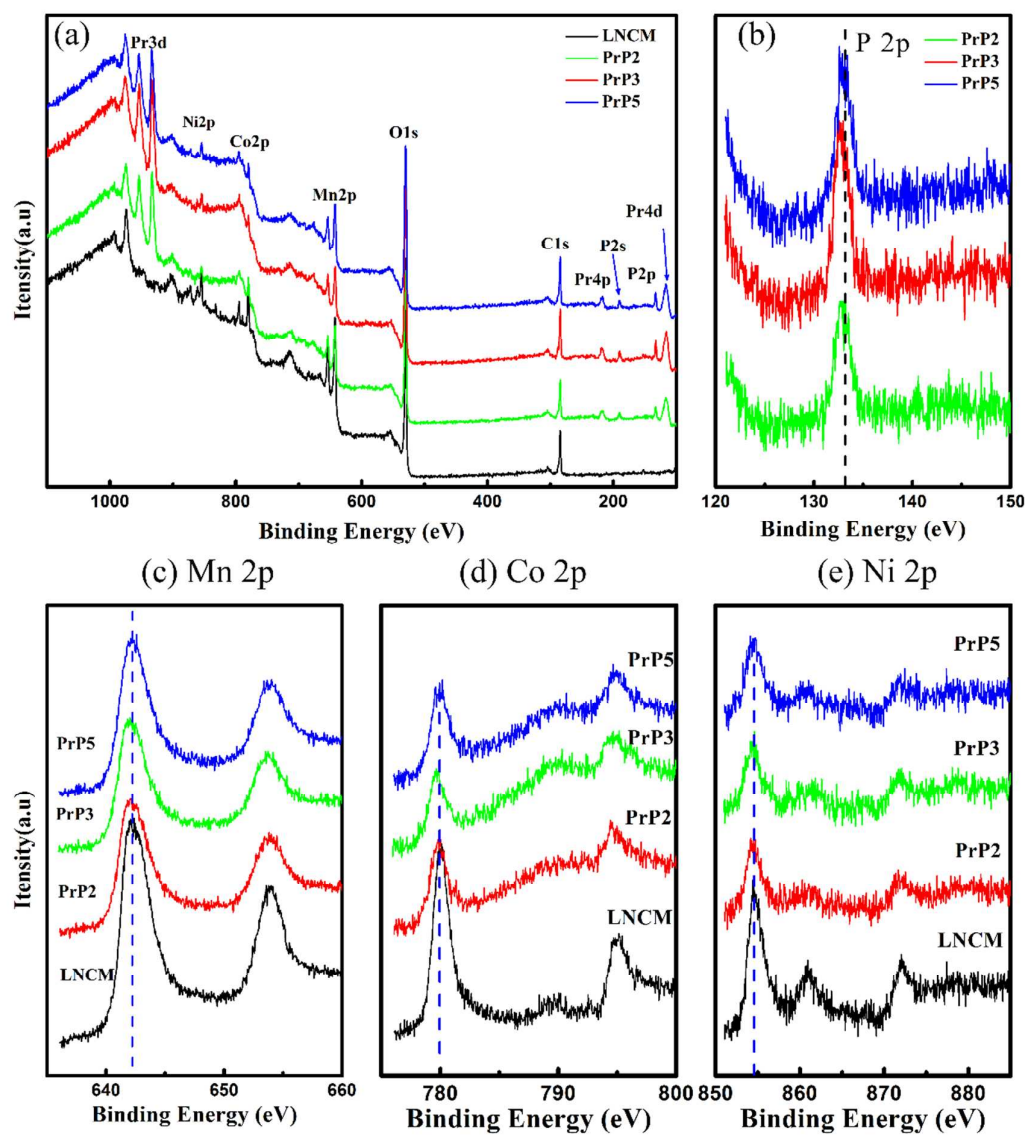


**Fig S3.** Raman spectra of the prepared samples LNCM and PrP3. Both two samples share the typical characterizations of layered lithium-rich materials.

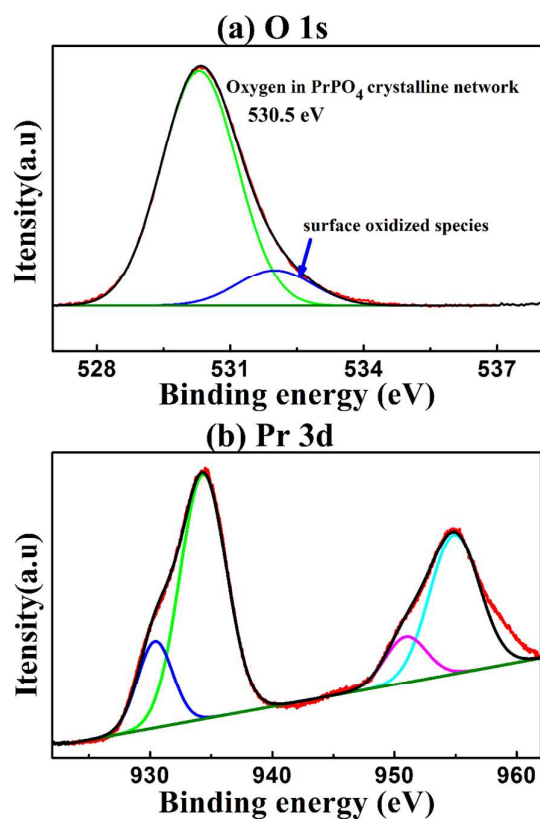


**Fig S4.** STEM and EDS characterization of the PrP3 sample: (a) STEM image and qualitative EDS mapping revealing the presence of (c) oxygen (magenta), (d) nickel (red), (e) cobalt (blue), (f) manganese (cyan), (g) praseodymium (cyan), (h) phosphorous (yellow) and (b) all of the above elements (mixed colors).

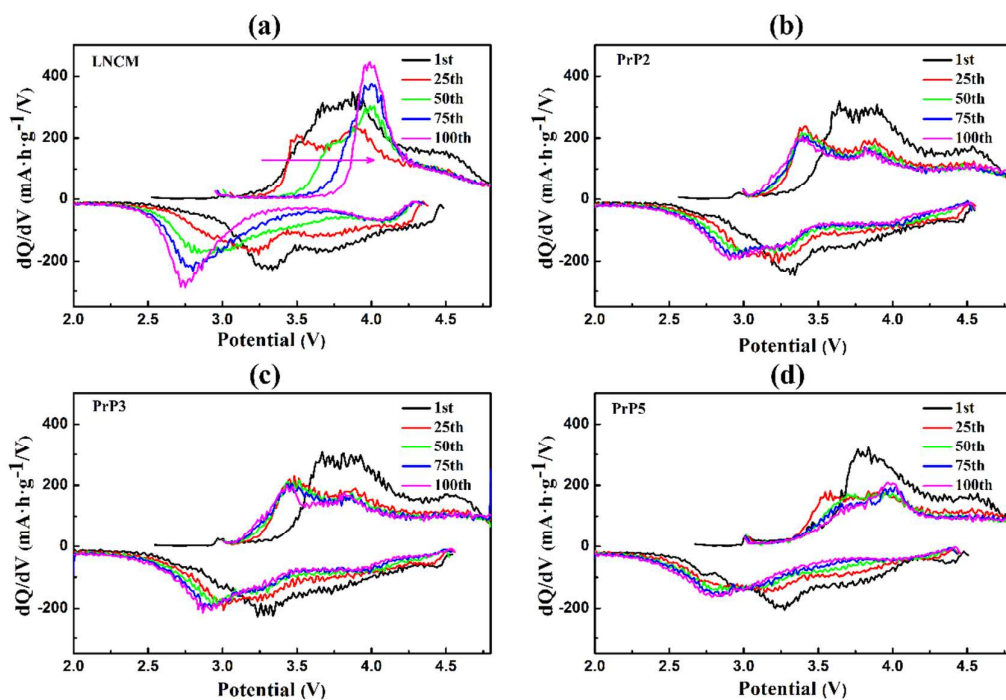




**Fig S5.** (a) XPS spectra of as-prepared LNCM, PrP2, PrP3 and PrP5; (b-e) the high-resolution XPS spectra of P 2p, Mn 2p, Co 2p, and Ni 2p.



**Fig S6.** XPS spectra for O1s (a) and Pr 3d (b) of the pure  $\text{PrPO}_4$  calcined at 450 °C.



**Fig S7.** Differential capacity vs. voltage ( $dQ/dV$ ) plots of (a) LNCM, (b) PrP2, (c) PrP3, and (d) PrP5 electrodes at different cycles during cycling corresponding to the data in Fig 10.

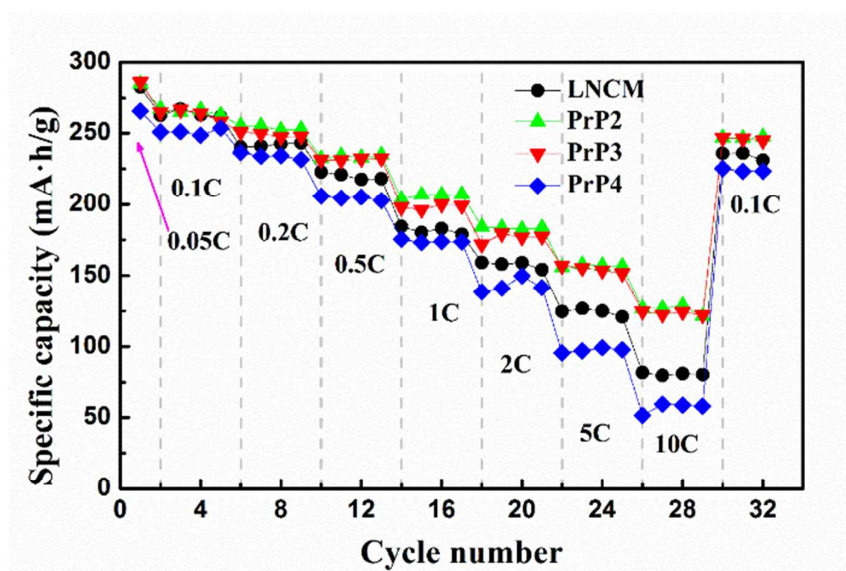
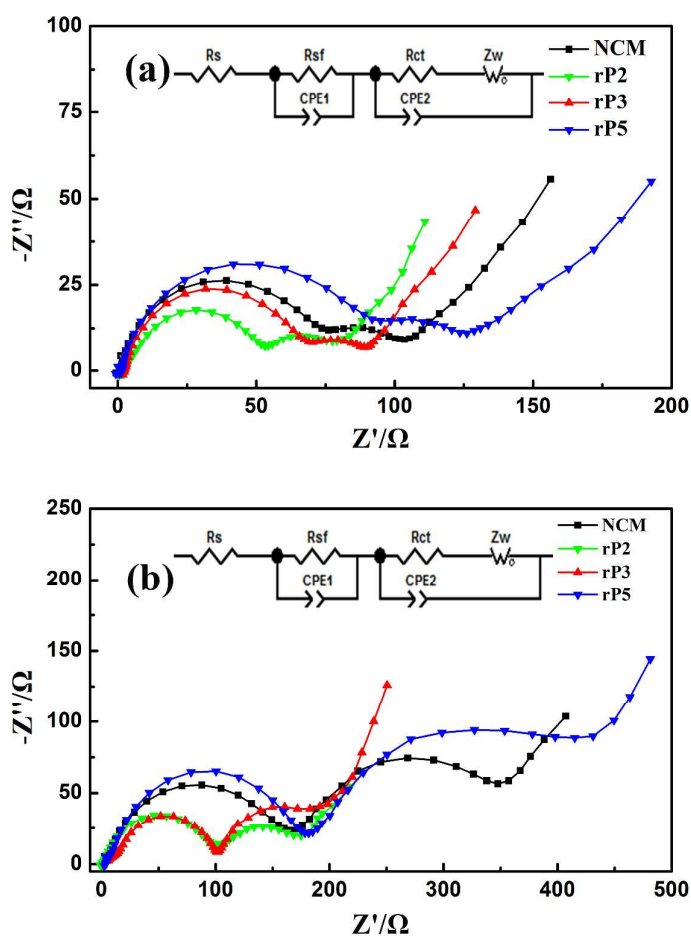


Fig S8. Rate capabilities of the prepared samples LNCM, PrP2, PrP3 and PrP5.



**Fig S9.** Electrochemical impedance spectra (EIS) of the prepared samples in (a) first cycle and (b) 51st cycle at 0.5C rate (inset is equivalent circuit). EIS were measured in the open-circuit mode when charged to 4.0V (vs Li/Li<sup>+</sup>).

**Table S1.** Fitted values of  $R_{sf}$  and  $R_{ct}$  for the prepared samples after the 1st, 51th cycles.

		LNCM	PRP2	PRP3	PRP5
1st	$R_{sf}/\Omega$	68.5	49.8	57.9	84.2
	$R_{ct}/\Omega$	52.2	24.3	34.7	40.8
51st	$R_{sf}/\Omega$	162.8	94.9	58.9	182.5
	$R_{ct}/\Omega$	207.3	84.5	90.5	174.2

## References

- (1) Li, J.; Li, J.; Yu, T.; Ding, F.; Xu, G.; Li, Z. Stabilizing the Structure and Suppressing the Voltage Decay of  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  Cathode Materials for Li-ion Batteries via Multifunctional Pr Oxide Surface Modification. *Ceram. Int.* **2016**, *42* (16), 18620–18630.