

Nanoporous $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as an ultra-fast charge cathode material for aqueous rechargeable lithium batteries

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Electronic Supporting Information (ESI):

1. Preparation of NCM and NP-NCM: The nanoporous $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was synthesized by a VGCFs-assisted sol-gel method. At first, VGCFs (from Showa Denko, Japan) were treated in concentrated nitric acid to remove some impurities and to endow their surface with hydrophilic groups such as $-\text{OH}$ and $-\text{COOH}$. These functional groups not only facilitate the dispersion of VGCFs in water but also serve as centers to combine metal ions with positive charge. Next, the acid-treated VGCFs (0.2g) were ultrasonically dispersed into 50 ml distilled water. Then a stoichiometric amounts of lithium acetate $[\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}](0.01\text{mol})$, manganese acetate $[\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}]$, and nickel acetate $[\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}]$ with the atomic ratio $\text{Li} : \text{Ni} : \text{Mn} : \text{Co} = 3 : 1 : 1 : 1$, were dissolved in the distilled water. After refluxing under vigorous stirring at $100\text{ }^\circ\text{C}$ for 6 h, the citric acid was mixed with that solution (the molar ratio of carboxylic acid groups in citric acid to metal ions was fixed at 1:1). Then ammonia was added slowly to this solution with constant stirring until pH of about 7-8 was achieved. In the presence of ethylene glycol, the resultant solutions were evaporated at $80\text{ }^\circ\text{C}$ until transparent gels were obtained. To remove water, the obtained mixture was dried under vacuum at $120\text{ }^\circ\text{C}$ overnight. The resulting gel was burned at $450\text{ }^\circ\text{C}$ for 6 h, then $750\text{ }^\circ\text{C}$ for 10 h in air. The rising rate of temperature was $3\text{ }^\circ\text{C min}^{-1}$. For comparison, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) was prepared via the same method without using VGCFs.

2. Material characterization: The X-ray diffraction (XRD) patterns were collected using a Rigaku D/MAX-IIA X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Scanning electron micrographs (SEM) were obtained by a Philip XL30 operated at 25 kV. Transmission electron micrographs (TEM) were got using a JEOL JEM-2010 transmission electron microscope. Nitrogen sorption-desorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (U.S.A.).

3. Electrochemical measurement: The electrodes were prepared by well mixing the samples, acetylene black and polytetrafluoroethylene in a weight ratio of 8:1:1. The mixture was pressed into a film, then dried at $120\text{ }^\circ\text{C}$ overnight. After drying, the film was cut into disks of about 1.5 mg (0.25 cm^2). These disks were pressed onto a Ni-grid at a pressure of 15 MPa to act as working electrodes. Activated carbon (AC, specific surface area of about $2800\text{ m}^2\text{ g}^{-1}$, purchased from Ningde Xinseng Chemical Industrial Co., Ltd.) electrodes were prepared in the same way as the NCM electrodes for cycling test. The cyclic voltammogram (CV) and the galvanostatic charge and discharge tests were performed in $0.5\text{ mol l}^{-1}\text{ Li}_2\text{SO}_4$ solution with a three-electrode cell, where a Ni-grid and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All electrochemical tests were carried out at $25\text{ }^\circ\text{C}$.

4. Physical characterization of VGCFs, NCM and NP-NCM:

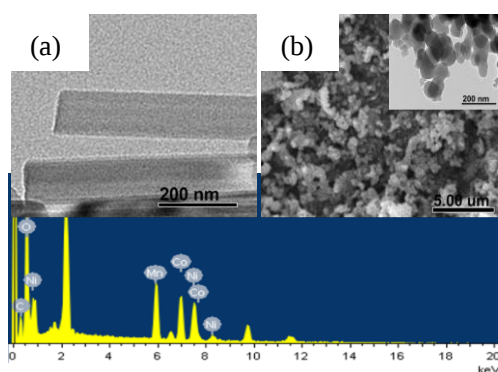


Fig.S1 (a) TEM micrograph of VGCFs after acid treating, (b) SEM and TEM (insert) micrographs of NCM, (c) EDX pattern of NP-NCM.

Vapour grown carbon fibers (VGCFs) are nano- to quasi-nano-sized fibers with a diameter ranging from 50 nm to 200 nm, which are produced by chemical vapor deposition (CVD) with transition metallic particles as the catalyst at high temperatures. They are characterized by highly preferred orientation of their graphitic basal plane parallel to the fiber axis and with annular carbon layers arranged like a tree ring structure.^{1,2} In contrast to multiwalled carbon nanotubes (MWCNTs), VGCFs are mechanically strong and not observably shortened or damaged by

ultrasonication because they have a diameter about one order higher than that of MWCNTs.² The $-\text{COO}^-$ of citric acid and VGCFs can chelate many metal ions such as Zn^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Mg^{2+} and Co^{2+} owing to its high negative charges on the surface.^{3, 4, 5}

EDX measurement for NP-NCM (Fig. S1 c) presents that the Ni : Co : Mn ratio was 0.31 : 0.33 : 0.33, indicating the composition of Ni/Co/Mn=1:1:1.

The Nyquist plots (Fig. S2e) of the NP-NCM and the NCM electrodes show a semicircle at mid-high frequency and a linear region at low frequency. It can be seen that the NP-NCM exhibits smaller surface charge transfer resistance compared to the NCM, an indication of faster Li-intercalation kinetics. This excellent property could be attributed to the inter-connected nanometer-sized pores in the NP-NCM. The presence of the interconnected pores means that the electrolyte can penetrate into the pores of the spinel to favor the fast transference of Li-ions.

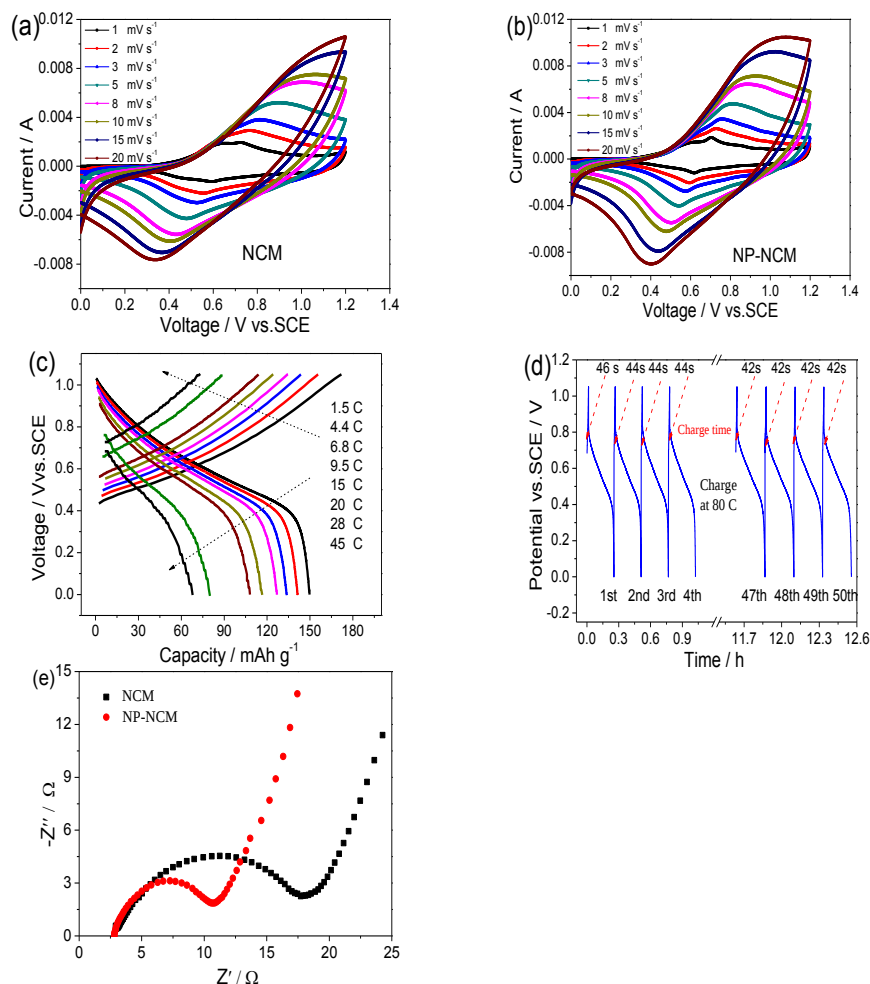


Fig.S2 CV curves of (a) NCM and (b) NP-NCM, (c) the galvanostatic charge and discharge curves of NCM, (d) charge/discharge curves of NP-NCM when charge at 80C and discharge at 3C, and (e) the Nyquist plots of the NP-NCM and NCM.

References:

- 1 M. Endo, Y.A. Kim, T. Hayashi, K. Nishimura, T. Matusita, K. Miyashita and M.S. Dresselhaus, *Carbon*, 2001, **39**, 1287
- 2 L. Sun, H. Guo, Z. Zhu, T. Guo and M. Peng, *RSC Adv.*, 2013, **3**, doi:10.1039/C3RA00116D.
- 3 L.J. Fu, H. Liu, C. Li, Y.P. Wu, E. Rahm, R. Holze and H.Q. Wu, *Prog. Mater. Sci.*, 2005, **50**, 881.
- 4 F. Shiba, R. Fujishiro, T. Kojima and Y. Okawa, *J. Phys. Chem. C*, 2012, **116**, 3394.
- 5 M. Adeli, R. Soleyman, Z. Beiranvand and F. Madani, *Chem. Soc. Rev.*, doi: 10.1039/c3cs35431h.