

# High Power Lithium-ion Battery based on Spinel Cathode and Hard Carbon Anode



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## ABSTRACT

Power performance of lithium-ion batteries (LIBs) is generally controlled by the Li<sup>+</sup> diffusion within crystalline framework of electrode materials, and thus nano-sized electrode materials with shortened diffusion length have been widely used to build high power LIBs. However, the undesired effects from nano-sized electrode materials, such as low tap density, low thermal stability and increased interface also discount the overall performance of LIBs. Accordingly, it is desired to develop high power LIBs with micro-sized electrode materials. Herein, we demonstrate that hard carbon displays fast Li-storage kinetics which is not controlled by Li<sup>+</sup> diffusion in the crystalline framework. Furthermore, it is found that micro-sized spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub> have high rate performance, owing to their three-dimensional channels for Li<sup>+</sup> diffusion. Finally, the micro-sized spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (or Li<sub>1.1</sub>Mn<sub>2</sub>O<sub>4</sub>) and micro-sized hard carbon are used as cathode and anode, respectively, to fabricate the full cells that exhibit supercapacitor-like high power performance. The achieved results point a way to develop high power LIBs besides nano-sizing electrode materials.

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## 1. Introduction

The charge storage of current lithium-ion batteries (LIBs) mainly depends on Li<sup>+</sup> intercalation/de-intercalation in electrode materials, and thus is controlled by the Li<sup>+</sup> diffusion within crystalline framework of electrode materials [1]. Accordingly, LIBs have to take hours to recharge when they run out. Synthesizing nano-sized electrode materials is one of the most efficient approaches to increase the charge/discharge rate (or power) of LIBs because of the shortened diffusion length and increased electrolyte/electrode interface [2–16]. However, nano-sizing also leads to low tap density, low thermal stability and aggravated decomposition of electrolyte at interface, which discounts the overall performance of LIBs. [17,18] Therefore, it should be desired to build high power LIBs using micro-sized electrode materials.

The Li<sup>+</sup> diffusion channels of electrode materials depend on their inherent crystalline framework. The diffusion channels of Li<sup>+</sup> can be classified as: one-dimensional (1-D) (e.g. olivine LiFePO<sub>4</sub>) [19,20], two-dimensional (2-D) (e.g. layer LiCoO<sub>2</sub>) [21] and three-dimensional (3-D) (e.g. spinel LiMn<sub>2</sub>O<sub>4</sub> and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>) [22,23].

The Li<sup>+</sup> diffusion length ( $L$ ) can be estimated as  $\sqrt{Dt}$ , where  $D$  and  $t$  are the diffusion coefficient and time, respectively. Obviously, the value of  $t$  decreases rapidly at high charge–discharge current. Therefore, the effective specific capacity rate will depend on the volume ratio ( $V_r$ ), and can be summarized:

$$V_r = \frac{r^n - (r - L)^n}{r^n} \quad (1)$$

Where  $r$  is the radius of the electrode active particle,  $n$  is the dimension of diffusion channels (1, 2 or 3). Without enough charge/discharge time ( $t$ ), the diffusion length  $L$  will be shorter than the radius of particle ( $r$ ), leading to limited utilization of electrode materials. According to equation (1), the utilization of electrode materials depends on the diffusion length ( $L$ ) and the dimension of diffusion channels ( $n=1, 2$  or  $3$ ). Obviously, the inherent high diffusion coefficient ( $D$ ) of electrode materials can increase the diffusion length ( $L$ ) in a special time, and thus increase the utilization of electrode materials. On the other hand, dimension of diffusion channels ( $n=1, 2$  or  $3$ ) of electrode materials can also affect the utilization. For example, if the diffusion length  $L$  is only  $0.3r$ , the corresponding utilizations are 30% for 1-D diffusion, 51% for 2-D diffusion and 67% for 3-D diffusion, respectively (equation 1). In other words, the electrode materials with typical 3-D diffusion channels have the potential to

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exhibit high rate performance even with micro-size. For example, the bulk  $\text{LiMn}_2\text{O}_4$  with three-dimensional diffusion channels has been successfully used as cathode in high power LIBs (i.e.  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  system) [24]. Furthermore, Ceder et al. have also demonstrated that micro-sized  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can show high rate performance [25].

Besides 3D-diffusion channels, fast kinetics could also make micro-sized electrode materials display high rate ability. Recently, it has been demonstrated that several nano-sized or nano-structured anode materials, such as  $\text{MoO}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$ , display pseudocapacitive  $\text{Li}^+$  intercalation, in which the charge storage within the crystalline framework of active materials is not controlled by  $\text{Li}^+$  diffusion [26–28]. These anode materials exhibit supercapacitor-like high rate ability and slope charge/discharge curves within a wide potential window, which is different from conventional battery electrode [29]. Are there micro-sized active materials with pseudocapacitive intercalation behavior? It should be the next interesting topic. Hard carbon has been widely investigated as a high rate anode material to replace conventional graphite anode [30]. Furthermore, Li-storage of hard carbon occurs in a wide potential window from 1.5 to 0 V (vs.  $\text{Li}/\text{Li}^+$ ). Therefore, it may be the next one showing pseudocapacitive intercalation behavior. However, its Li-storage kinetics has never been investigated up to now.

In present work, the electrochemical properties of micro-sized hard carbon (HC), spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) and  $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$  (LMO) were investigated. It is demonstrated that micro-sized HC exhibits typical pseudocapacitive  $\text{Li}^+$  intercalation and inherent high rate performance. On the other hand, owing to the 3-D diffusion channels, micro-sized spinel LNMO and LMO display high rate performance. Finally, micro-sized LNMO (or LMO) and HC were used as cathode and anode, respectively, to build full cells with high energy density and supercapacitor-like high power density.

## 2. Experiment

### 2.1. Synthesis of electrode materials

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) powder was synthesized by a solid-state method. Stoichiometric amount of  $\text{Li}_2\text{CO}_3$ ,  $\text{NiCO}_3$ , and  $\text{Mn}_3\text{O}_4$  was ground for 0.5 h in an agate mortar. After drying, the precursor was calcined in air at  $650^\circ\text{C}$  for 5 h, then calcined in  $\text{O}_2$  at  $900^\circ\text{C}$  for 12 h and kept at  $750^\circ\text{C}$  for 24 h. Li-rich spinel ( $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ , LMO) was also synthesized by solid-state method. In typical synthesis, stoichiometric amount of  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  were mixed together and reacted at  $530^\circ\text{C}$  for 5 h, followed by heating at  $850^\circ\text{C}$  for 24 h in air, and then the sample was cooled over a three-hour period. Commercialized hard carbon (HC) was used as electrode material without further treatment.

### 2.2. Materials Characterization

XRD patterns of LNMO, LMO and HC were characterized on a Bruker D4 Endeavor X-ray diffractometer (XRD) employing  $\text{Cu-K}\alpha$  radiation (40 kV, 35 mA). Field emission SEM (FE-SEM s-4800 and Nova NanoSem 450) was used to collect SEM images. TEM experiments were carried out on a JEOL 2011 microscope (Japan) operated at 200 kV. Nitrogen sorption isotherms were measured at 77 K using a Quantachrome ASiQwin analyzer (USA). The specific surface areas ( $S_{\text{BET}}$ ) were calculated by the Brunauer-Emmett-Teller (BET) method.

### 2.3. Electrochemical Investigation

To prepare the anode, hard carbon was first mixed with acetylene black carbon and polyvinylidene fluoride in a weight

ratio of 90:5:5 employing N-methyl-2-pyrrolidone (NMP) as solvent to form a slurry. Cu foil was used as the current collector, on which the slurry was pasted. The cathode was prepared by brushing a NMP-based slurry consisting of 85 wt % of active material (LNMO or LMO), 10 wt % of Super P carbon black, and 5 wt % of polyvinylidene fluoride binder on Al foil. Finally, the electrodes of anode and cathode were dried at  $80^\circ\text{C}$  for 24 h in vacuum oven to remove solvent (NMP). CR 2016 coin-type cells were assembled to fabricate half cells and full cells in an argon-filled glove box. Celgard 2300 film was employed as the separator. A solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 by vol.) was selected as the electrolyte. For half cells measurements that use lithium foil as counter and reference electrode, the mass loading of electrode materials (LNMO, LMO and HC) was controlled at  $\sim 2\text{ mg cm}^{-2}$ . For full cells investigation, the mass ratios of HC: LNMO and HC: LMO were optimized to be 1: 2 (HC:  $2\text{ mg cm}^{-2}$ /LNMO:  $4\text{ mg cm}^{-2}$ ) and 1: 2.5 (HC:  $1.5\text{ mg cm}^{-2}$ /LNMO:  $3.75\text{ mg cm}^{-2}$ ), respectively. Cyclic voltammetry (CV) experiments were performed on a PARSTAT MC PMC-500. Galvanostatic charge/discharge measurements were carried out on Hokuto Denko Battery charge/discharge system HJ series controlled by a computer.

## 3. Results and discussion

SEM and TEM images of HC are shown in Fig. 1. As shown in Fig. 1a, the morphology of HC particles is irregular, and the average

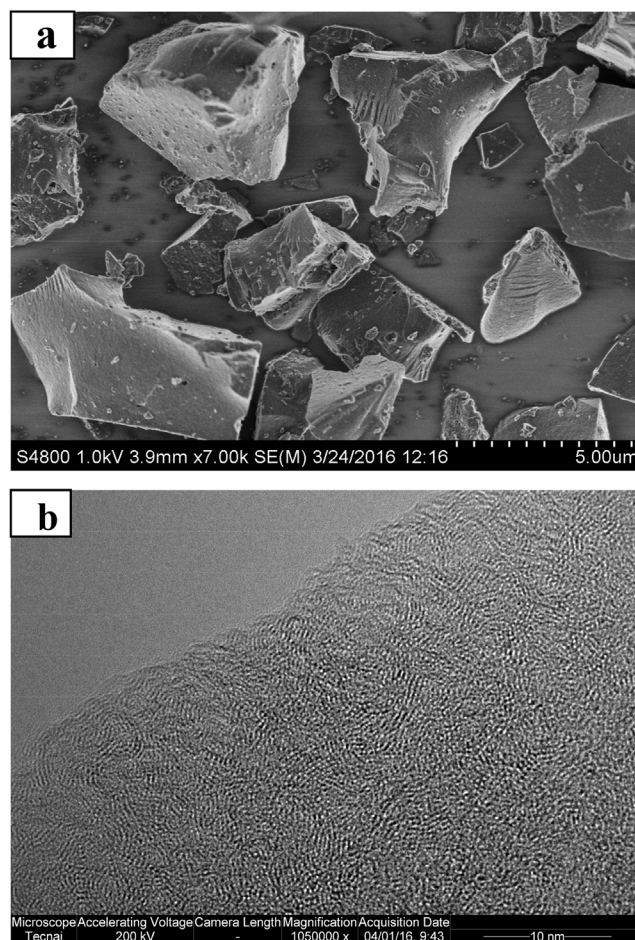


Fig. 1. Characterization of hard carbon (HC). (a) SEM of hard carbon, (b) TEM of hard carbon.

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