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Soft-contact conductive carbon enabling depolarization of LiFePO₄ cathodes to enhance both capacity and rate performances of lithium ion batteries

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ABSTRACT

HIGHLIGHTS

• The mechanism of conductive nanocarbons enhance LIBs's performance is proposed.

- Three types of nanocarbons and related performances in LFP electrodes are studied.
- SCC can generate much larger contact area than that of HCC.
- LFP nano-crystals wrapped in SCC perform significantly enhanced.
- Combined experiments with multiphysics simulation, the mechanism is elaborated.

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Keywords: Soft-contact conductive carbon LiFePO4 Depolarization Multiphysics simulation Li-ions batteries Conductive nanocarbons generally are used as the electronic conductive additives to contact with active materials to generate conductive network for electrodes of commercial Li-ion batteries (LIBs). A typical of LiFePO₄ (LFP), which has been widely used as cathode material for LIBs with low electronic conductivity, needs higher quantity of conductive nanocarbons to enhance the performance for cathode electrodes. In this work, we systematically studied three types of conductive nanocarbons and related performances in the LFP electrodes, and classify them as hard/soft-contact conductive carbon (named as H/SCC), respectively, according to their crystallite size, surface graphite-defect, specific surface area and porous structure, in which SCC can generate much larger contact area with active nano-particles of cathode materials than that of HCC. It is found that LFP nanocrystals wrapped in SCC networks perform significantly enhanced both capacity and rate performance than that in HCC. Combined experiments with multiphysics simulation, the mechanism is that LFP nanoparticles embedded in SCC with large contact area enable to generate higher depolarized effects with a relatively uniform current density vector (i_s) and lithium flux vector (N_{Li}) than that in HCC. This discovery will guide us to how to design LIBs by selective using conductive carbon for high-performance LIBs.

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1. Introduction

Rechargeable lithium batteries (LIBs) have been widely used for portable electronics, energy storage devices, hybrid electric vehicles (HEVs) and electric vehicles (EVs) [1–4]. High energy density and high power density of electrodes are important to be continuously improved for applications of LIBs. Energy density of LIBs depends on both capacity and potential of electrodes, which relates to lithium-storage properties and effective migration of Li-ions in active materials of electrodes [5]. High power density of LIBs need electrodes to perform high energy density with high current density, which requires cathode and anode electrodes to be able to achieve high charge/discharge rate capability. The rate performance of an electrode depends on the kinetics of the deintercalation/intercalation of Li-ions and loss/gain of electrons at the contacted interface. Various methods to enhance the Li







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intercalation rate in the cathode materials have been already well developed, for example, to scale particles to nano-size to shorten the Li-ion diffusion path in olivine-based LiMPO₄ (M = Fe, Mn, Co) [6], to introduce more Ni^{2+} content or enlarging the Li slab space to decrease the diffusion energy barrier in layered LiNixMnyCo₂O₂ (NMC) [7.8] and to tune the temperature to improve the Li-ion diffusion in Li₂MSiO₄ (M = Fe. Mn. Co. or Ni) [9]. For example, olivine LiFePO₄ (LFP), which is one of the most used as the cathode material in EV LIBs, has the low electronic and Li-ionic conductivity. In order to improve the capacity and rate performance, LFP nanoparticles are generally coated nanocarbons to enhance the transport of electrons [10]. In addition, the Li de-intercalation/ intercalation rate also is controlled by migration of Li ions to or from the interfaces of active nano-particles [11]. For example, optimized solid-liquid interface, e.g. "Janus" solid/liquid interface of LFP in aqueous electrolyte, can achieve ultrahigh fast chargingdischarging rate (600 C reaching 72 mA h g⁻¹ energy storage) [12]. Based on the above discussion, achieving both high capacity and high charge-discharge rate performance requires coordination of improvements of interfaces for both Li-transport and electronic conduction.

The majority of cathode active materials, such as NMC, LFP, and Li₂FeSiO₄, belong to semiconductor with low electronic conductivity. These active particles need to contact with conductive network closely to depolarize for cathode electrodes. In previous work, we demonstrated strategies to achieve depolarization effects by forming a stand-alone electrode to embed NMC active materials into the carbon nanotubes (CNT) network [13], and by preparing hybrid electrode of Li₂FeSiO₄ nanoparticles with chemically bonding on high conductive graphene network to lead to interface depolarization to enhance rate and capacity performances of LIBs [14,15]. For commercial LIBs, conductive-nanocarbon (CNC) is generally used as the electronic conductive additive to contact with active materials to improve interface electronic/Li-ions conductive due to its low cost, high electronic conductivity and favorable thermodynamic stability [16,17]. In an electrode, CNC links together to generate conductive network, which can facilitate fast current flow with minimum resistance through the entire electrode to reduce the polarization effects and to improve electrochemistry performance of active materials [18-23]. On another hand, it is well known that LFP has been intensively investigated as promising cathode material for EV LIBs owing to its high capacity, excellent cycle life, thermal stability, environmental benignity and low cost [24–28]. However, the low electronic and ionic conductivities of LFP seriously limit charge transport rates in these materials. The nano-LFP wrapped in conductive carbon networks is popular as a simple and effective way to improve electronic and ionic transport kinetics, but the mechanism of enhanced LIB performance needs to find out.

In this work, we systematically study the depolarization effects of three types of conductive nanocarbons (sphere, tube and porous nanocarbons) on LFP cathodes. The main focus includes the role of structure and morphology of these nanocarbons and polarization/ depolarization effects of small/large contact area between nanocarbons and LFP nanoparticles, which can lead to decrease/increase both capacity and rate performance of LFP cathodes. According to sp²/sp³ hybrid, crystallite size, surface defect, morphologies, specific surface area and porous structures of these nanocarbons, and contact effects with LFP, we classify for the first time conductive nanocarbons as hard/soft-contact conductive carbons (H/SCC), respectively. One of three conductive carbons with a typical of porous with hair morphologies is classified as SCC, which is soft and able to make surface contact to LFP nano-particles of cathode with large contact area due to its high sp^2 hybrid (~80%), numerous surface-defect, small crystallite size ($L_a \approx 4 \text{ nm}$), and large specific surface area (>1000 m² g⁻¹) composed by curled graphene-like with mesoporous pores. On the contrary, another of three conductive carbons with morphology of nanosphere is classified as HCC, which is hard with only point contact to LFP with small contact area. Carbon nanotube (CNT) shows contact effects with more partial of HCC with less partial of SCC. By using multiphysics simulation, we demonstrated the contact effect of HCC and SCC with LFP nanoparticles in cathode electrodes, showing that large contact area between LFP and SCC can create relatively uniform current density vector (*i*_s) and lithium flux vector (*N*_{Li}) so as to minimize polarization for LFP cathodes.

2. Results and discussion

Morphology and structure characteristics of three different nanocarbons, such as HCC, CNT and SCC are shown in Fig. 1a-c. Fig. 1a shows the transmission electron microscopy (TEM) image of a kind of HCC with the average dimeter of ~50 nm. High resolutiontransmission electron microscopy (HRTEM) (inset of Fig. 1a) image displays HCC has a "hard" nano-ball to joint together with coralloid beaded structure constructed by approximate graphite layer with interlamellar spacing of 0.35 nm, which can be expected to have good electron mobility in a single or jointed HCC particles. Fig. 1b shows that the diameter of CNT is ~15 nm and interlamellar spacing (inset of Fig. 1b) is 0.34 nm, in which electrons can transmit favorably along the direction of carbon nanotubes. Fig. 1c shows that SCC has average diameter of ~10 nm of with some turbostratic structures, which are similar to curled graphene to be randomly stacked and formed with mesoporous pores indicated by HRTEM (inset of Fig. 1c). The interlamellar spacing of crystallite stands in the range of 0.34–0.41 nm, corresponding the broadening (002) peak in XRD profiles (Fig. 1d). In addition, the crystallite diameter $(L_a = 1.84\lambda/\beta_{100}\cos\theta_{100})$ and height $(L_c = 0.89\lambda/\beta_{002}\cos\theta_{002})$ [29,30] of the nanocarbons can be obtained by calculating and analyzing the X-ray diffraction, the results are shown in Table 1. The smaller L_a of SCC indicated that smaller graphite crystallite size, which is in accordance with the calculated results $(L_a = C(\lambda_L)/(I_{D1}/I_G)^{-1})$ [31,32] from the integrated intensities of the disorder-induced D₁ and G bands (I_{D1}/I_G) in Raman spectra (Fig. 1e). Two representative atomic symmetries and hybridization of carbon materials are threefoldcoordination (sp^2) as in graphite or fourfold-coordination (sp^3) as in diamond [33,34]. Compared to the ambiguity of C1s banding fitting in X-ray photoelectron spectroscopy (XPS) to evaluate the carbon hybridization, the width (marked as D parameter) of the first derivative of C-KLL spectrum in X-ray excited Auger electron spectroscopy (XAES) is a generally accepted method to determinate the relative amounts of sp²/sp³ ratio [35–37]. Fig. 1f shows the first derivative of the C-KLL spectrum of diamond, HCC, CNT, SCC and Graphite. The D parameter of diamond, HCC, CNT, SCC and graphite is 13.0, 18.6, 20.2, 19.2 and 21.0 eV, respectively, which means that the amounts of sp^2 -type carbon of them are 0%, 70.0%, 90%, 77.5% and 100%. It is well known that the integrated area ratio $A_{(G+D1)}$ and A(D2+D3) in Raman spectrum can also be used to estimate the relatively content of the sp²/sp³-type carbon [38,39]. The sp² type carbon content of HCC, CNT and SCC decided from Raman bands (Fig. 2a) is 73.1%, 84.5%, and 77.7%, respectively, which is in accordance with the results of XAES of C-KLL spectra. The electronic conductivity of these nanocarbons samples tested by a four-probe method (Fig. S1, Supporting Information) is shown in Fig. 2b, which shows that SCC has better electronic conductivity than HCC and CNT. The ratio of D₃ band and G band is always used to estimate the relatively content of the defect structure (C_{defect}) outside the plane of aromatic layers in carbon materials [32,39-41]. The fitted results of Raman spectra (Table 1) show that the CNT have lesser defect structure, while more defect structure resided are found in



Fig. 1. Morphology and structure characteristics of three kinds of nanocarbons: SEM and HRTEM (inset) images of (a) HCC, (b) CNT, (c) SCC, (d) XRD profiles, (e) Raman spectra and (f) first derivative of C-KLL spectra of HCC, CNT and SCC (Diamond and Graphite are used as reference).

| Table | e 1 | |
|-------|-----|--|
| - | | |

| Structure characteristic | parameters o | f three | kinds of | f nanocarbons: | HCC. | CNT and | I SCC. |
|-----------------------------|--------------|---------|------------|----------------|------|---------|--------|
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| Nanocarbons | d ₀₀₂ (nm) | L _c (nm) | D ₁₀₀ (nm) | L _a (nm) | C _{defect} (%) | C _{sp2} (%) | BET $(m^2 g^{-1})$ |
|-------------|-----------------------|---------------------|-----------------------|---------------------|-------------------------|----------------------|--------------------|
| НСС | 0.35 | 2.14 | 0.210 | 4.67 | 34.5 | 70.0 | 54.3 |
| CNT | 0.34 | 2.85 | 0.212 | 8.72 | 5.6 | 90.0 | 190.4 |
| SCC | 0.36 | 1.74 | 0.210 | 4.01 | 34.8 | 77.5 | 1318.5 |

HCC and SCC. However, HRTEM images show that the defect structures for HCC are inside of the spheres. So the HCC have hard contact with the active materials, which are named as hard-contact

conductive carbon (HCC). Different from HCC, the graphite crystallite in SCC are linked by numerous surface defect carbon, forming much more porous structure and larger specific surface area



Fig. 2. (a) D-parameter versus percentage of sp² (b) electronic conductivity, (c) specific surface area and pore size distribution (inset) of HCC, CNT and SCC, (d) SEM images of LFP100@SCC electrode, (e) charge-discharge curves at 0.2 C and (f) rate capacities of the LFP100(50)@HCC, LFP100(50)@CNT and LFP100(50)@SCC electrodes.

(Fig. 2c), resulting in SCC is "soft" and easy to contact to the active materials (Fig. 2d) with larger contact area, which can reduce contact resistance and enhance conductivity for the electrode (Fig. S2, Supporting Information). Therefore, that is why we can classify this kind of nanocarbon as soft-contact conductive carbon (SCC). CNT performs features between HCC and SCC. HCC, CNT and SCC will be used for further investigation of electrochemical performance with different sizes of LFP nano-particles as active materials in the electrodes of LIBs as below.

The electrode performances of LFP (the characterization of LFP shown in Figs. S4 and S5, Supporting Information) with two different crystal sizes of 100 nm and 50 nm wrapped in SCC networks (named as LFP100(50)@SCC, 100(50) related 100 nm and 50 nm, respectively, and same type of definition used below) were investigated by using coin-type Li cells. For comparison, the electrodes with LFP wrapped in HCC and CNT networks (named as LFP100(50)@HCC and LFP100(50)@CNT) were also prepared and electrochemically tested. The composite electrodes were cycled at various charge/discharge rates ranging from 0.2 to 10 C $(1 \text{ C} = 170 \text{ mA g}^{-1})$ over a potential window of 2.0–4.2 V. In order to evaluate fairly the electrochemical performances of LFP, the capacitances contribution of HCC, SCC and CNT were deducted by using capacitance curve fitting and equal voltage dots taking, respectively (Fig. S6, Supporting Information). Typical galvanostatic profiles of LFP100(50)@SCC, LFP100(50)@HCC and LFP100(50) @CNT at 0.2 C are shown in Fig. 2e, respectively. The discharge curves have a dominant plateau at about 3.4 V, which is attributed to Fe²⁺/Fe³⁺ redox [42]. Compared to LFP100(50)@HCC and LFP100(50)@CNT, LFP100(50)@SCC exhibits a longer plateau and a slightly reduced difference between charge and discharge voltage peaks in CV measurement (Fig. 4a), which means decrease of over potential with reduction of polarization. Fig. 2f further shows the differences of rate capabilities of these samples. At the rates of 0.2, 0.5, 1, 2, 5, and 10 C, the corresponding discharge capacities are 155(162) to 148(159), 139(153), 130(144), 115(125) and 100(110) mAh g^{-1} for LFP100(50)@SCC, versus 141(142) to 131(141), 121(136), 110(126), 93(105) and 76(82) mAh g^{-1} for LFP100(50)@HCC, respectively. Obviously, the LFP100(50)@SCC electrodes exhibit much better rate capability than LFP100(50)@CNT and LFP100(50)@HCC. Furthermore, it has been proved that SCC can also enhance electrochemical performances of other cathodes, such as commercial LiCoO₂ (Fig. S7, Supporting Information) and Li₂Fe-SiO₄/C nanocomposites (Fig. S8, Supporting Information), indicating the generality of using SCC as an effective additive to electrodes.

Fig. 3a shows the rate capacities of different LFP100@nanocarbon electrodes within 200 cycles at 10 C. It can be observed that the discharge capacity of LFP100@SCC is 96 mAh g^{-1} , which is higher ~8 mAh g^{-1} than LFP100@CNT electrode, and higher ~26 mAh g⁻¹ than LFP100@HCC electrode. Note that a long trailing in discharge curves usually results from the interface lithium storage as extra-capacity with lower voltage [23]. However, the corresponding discharge curves (Inset of Fig. 3a) shows that more capacity of LiFePO₄ with SCC is mainly located in the voltage platform part rather than in trailing parts. The same electrochemical features are performed in LFP50@SCC electrode (Fig. S9, Supporting Information). These experiment results prove that more lithium ions can spread out from the internal LFP nano-particles, rather than from the interface. What mechanism results in more lithium ions spreading out from the LFP internal in LFP@SCC electrodes? Since the same LFP active materials were introduced into the electrodes, its prominent rate capacity could be mainly ascribed to the role of unique SCC with large contact area. Fig. 3b-i shows that the contact model of the HCC with the agglomerated LFP particles (inside single particle size about 100 nm) belongs to single point contact (the similar model of LFP@CNT is shown in Fig. S10, Supporting Information). However, the SCC is different from the HCC, which is soft and easy to contact to LFP with large area due to the



Fig. 3. (a) Cycle capacities of different LFP100@nanocarbon electrodes within 200 cycles at 10 C, inset is the corresponding charge-discharge curves at the 50th cycle, (b) contact types of agglomerated LFP (100 nm) particles with (i)HCC and (ii)SCC in electrodes, which are approximately equal to the effective contact area with diameters(ϕ) of (i)4 and (ii) 25 nm in lithium ion battery using multiphysics. (c) the simulated current density vectors (*i*_s) and (d) potential distributions within LFP at 80 s (voltage platform) for the electrodes with (i)HCC and (ii)SCC.

numerous defect structures and large specific surface area. The contact model of the SCC with LFP particles belongs to surface contact (Fig. 3b-ii).

In order to investigate the mechanism of excellent electrochemical performance of LFP@SCC electrodes, multiphysics simulation of LIBs based on the LFP electrodes in experiment was proceeded. (Detailed simulated models can be seen in part S3, Supporting Information). In the simulation model, the electrode reaction occurs at the boundary of electrode and electrolyte, the theory of general mass balance for the diluted species and current distribution is used. Parameters are selected as the 100 nm of crystal size of LFP100 based on the average size calculated from XRD, around 50% of electrode porosity according to the experiment value, and the capacitances of nanocarbons to be ignored in the simulation model according to the experiment (Fig. S6, Supporting Information). We select hard-contact effect of HCC with LFP corresponded as a small contact area ($\pi^* 2^* 2 \text{ nm}^2$) like a kind of pointcontact, and soft-contact effect of SCC with LFP corresponded as a large contact area ($\pi^*25^*25 \text{ nm}^2$) like a kind of surface contact, from which the electrons can flow fast with less resistant. Preliminary simulation results show that the contact effect plays the key role for the excellent capacity and rate performance of LFP@SCC electrode, while the influence of conductivity is very limited (Figs. S19–21, Supporting Information).

For example, Fig. 3c shows the simulated discharge current density vector (i_s) at 80 s (other time shown in Fig. S14, Supporting

Information), in which all electron-streams are ended at the contact area, and the larger contact area ($\pi^*25^*25 \text{ nm}^2$) of LFP@SCC performs a relatively uniform current density vector compared with small contact area ($\pi^*2^*2 \text{ nm}^2$) of LFP@HCC. Meanwhile, the current density causes the change of the inducted potential ($V = \delta \cdot i_s$). Fig. 3d shows potential distribution at 80s (other time shown in Fig. S15, Supporting Information). The potential inside LFP@SCC drops only 0.04 mV over a large potential induction radius (r = 80 nm), while that inside LFP@HCC drops 0.14 mV over a small potential induction radius (r = 4 nm), indicating that the inducted potential distribution in LFP@SCC is more uniform than that in LFP@HCC, meaning smaller polarization in LFP@SCC. The depolarization appearance in LFP@SCC is further observed in CV curves (Fig. 4a). It can be seen that the LFP@SCC electrode has a narrow charge/discharge peak separation. Especially, compared to the LFP@HCC and LFP@CNT electrodes, the LFP@SCC electrode has a faster speed to arrive the peak vertices, resulting in anodic peaks deviate toward higher potential, and cathodic peaks deviate toward lower potential.

The rate capacity of LFP in LIBs depends on the kinetics of lithium diffusion and interface reaction. For same type of solidelectrolyte interface, the kinetics of interface reaction is similar. Hence, we can mainly attribute the different rate performance to Liion diffusion properties. Fig. 4b shows the simulation of the diffusion lithium flux vector (N_{Li}) at axial section within LFP at 80 s (other time shown in Fig. S16, Supporting Information). For



Fig. 4. (a) CV curves of different LFP100(50)@nanocarbon electrodes at 0.3 mV s⁻¹, (b) the lithium flux vectors (*N*_{*li*}) and (c) lithium ion distributions within LFP at 80 s (voltage platform) for the electrodes with (i)HCC and (ii)SCC, (d) the comparison of tested and simulated discharge curves of LFP100@H/SCC at 10 C.

LFP@HCC, the N_{Li} concentrates in the lower and upper region, deficiency in the middle part, resulting an unbalanced lithium concentration distribution (Fig. 4c-i and Fig. S17, Supporting Information) because of the fast potential drop with Li intercalation in the closed contact zone of LFP@HCC, and the slow potential drop in the remote zone (Fig. 3d-i and Fig. S15, Supporting Information), indicating that the capacity can be not effectively performed in the "small contact area" of LFP@HCC with the same diffusion coefficient, as a result that the power and capacity characteristics are seriously reduced at high charging/discharging rate. In contrast for the "large contact area" of LFP@SCC, the N_{Li} is separated uniformly from the center to the border of LFP, indicating a more balanced spatial distribution (Fig. 4c-ii) due to the potential drop with Li intercalation gently over very wide range (Fig. 3d-ii), as a results that the difference of concentration of lithium ions becomes less to benefit for achieving high-rate performance than that of LFP@HCC.

The simulated discharge curves of LFP@H/SCC at 10 C are shown in Fig. 4d (detailed discharge information shown in Fig. S18, Supporting Information). It can be seen that the simulated discharge capacities are very close to the tested capacity. Compared to LFP@HCC, the discharge capacity of LFP@SCC at the voltage platform part increase ~14 mA h g⁻¹, which has the same increase trend with the experimental data, so that the selected contact area of π^*2^*2 nm² for LFP@HCC and π^*25^*25 nm² for LFP@SCC for the simulation is quite reasonable. Thus, due to the contact effect, the LFP particle point-contacted by HCC with small contact area has unbalanced current density with more polarization effect and more voltage dropping, leading to unbalanced Li intercalation rate over the particle surface, unbalanced Li distribution inside LFP particles, all of which result in the lower capacity in LFP@HCC electrode. However, LFP particle wrapped in SCC with the large surface contact area can balance current density to make the Li ion intercalation uniformly over the particle surface, as a result the capacity and rate performance of the battery can be enhanced.

3. Conclusions

In summary, we classify for the first time conductive nanocarbons as SCC with a typical of porous with hair morphologies to be soft and able to make large surface contact to LFP nano-particles of cathode. HCC like a hard-ball to make only point contact to LFP with small contact area, and CNT with more partial of HCC with less partial of SCC. Compared with HCC, SCC can significantly enhance the capacity and rate capacity of LFP electrode, the enhanced capacity is mainly performed in the voltage platform part rather than in trailing parts during charge-discharge process, indicating that more lithium ions can spread out from the LFP internal. A multiphysics simulation of LIBs verified that the main reason was attributed to the "contact effect" between LFP and SCC or HCC. Large contact area between LFP and SCC can significantly enhance rate capacity with a relatively uniform current density vector (i_s) and lithium flux vector (N_{Li}) , which produce sensitive potential induction and uniform lithium concentration distribution within LFP. This discovery will guide us to design high-performance electrodes of LIBs with high energy and power densities for EV and HEV applications.

4. Materials and methods

4.1. Materials

Hard-contact conductive-carbon (HCC) was purchased from Li Yuan Li-ion battery Technology Center (Shanxi, China), Carbon nanotubes (CNT) from the Shenzhen Dynanonic Co., Ltd (Shenzhen, China) and soft-contact conductive-carbon (SCC) from Shanghai CuiKe Chemical Technology Co., Ltd (Shanghai, China), LFP100 (LiFePO₄ with mean grainsize of 100 nm) was purchased from Shenzhen BTR New Energy Technology Co., Ltd (Shenzhen, China), LFP50 (LiFePO₄ with mean grainsize of 50 nm) from the Shenzhen Dynanonic Co., Ltd (Shenzhen, China).

4.2. Characterizations

X-ray diffraction data were collected with a Bruker D₈-Advance diffractometer (40 KV, 40 mA Cu K_{α}, λ = 1.5418 Å, resolution 0.02°), Scanning electron microscopy (SEM) images were taken on a ZEISS SUPRA[®]55 field emission SEM instruments and Transmission electron microscope (TEM) imaging and High resolutiontransmission electron microscopy (HRTEM) were carried out on a FEI Tecnai G2F30. Raman Spectra were collected using a Horiba iHR320 in the 800–2000 cm^{-1} range with a using an Argon laser $(\lambda = 532.05 \text{ nm})$. X-ray excited Auger electron spectroscopy (XAES) were collected using a Thermo Fisher ESCALAB 250X, C KLL acquisition conditions: Pass energy = 100 eV, step size = 0.5 eV, 100 scans, scan range binding energy = 1190-1246 eV, with charge neutralization on, the specific surface area and pore size distribution were analyzed by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption measurement by a Micromeritics ASAP 2020 HD88. Electronic conductivity was tested by the KDJ-1A fourpoint probe instrument of Guanzhou Kunde Technology Co. Ltd.

4.3. Electrochemical measurements

The electrochemical properties were tested with 2016-type coin cells assembled in a glove box filled with pure argon. Lithium pellets were used as the anodes, a 1.0 M solution of LiPF₆ in ethylene carbonate/dimethyl carbonate (1/1) was used as the electrolyte, Celgard 2400 polypropylene as separator and the cathode electrodes were produced with 70% active material, 20% nanocarbons (HCC, CNT, SCC) and 10% poly-tetrafluoroethylene binder. The loading mass of the active material in the electrode is ~2 mg (thickness: ~ 15 μ m, area: 0.785 cm²). Galvanostatic charge/ discharge measurement was performed with a LAND CT2001A multichannel battery testing system at 25 °C. Cyclic voltammetry (CV) was tested with a CHI 660e electrochemical workstation.

4.4. Multiphysics simulations

The simulation process is performed by the COMSOL Multiphysics 5.0. The exchange current density is related to the rate performance of LIBs, which is the sum of Faradaic (electrode reaction) components. The total current at discharge rate of 10 C ($1 C = 170 \text{ mAh g}^{-1}$) is computed using the flowing equation:

$$i_{total} = \frac{C \cdot V_{LFP} \cdot \rho \cdot Capacity}{3600} \tag{1}$$

where V_{LFP} is the volume of the LFP, ρ is the density of LFP, *Capacity* is theoretical capacity and *C* is the discharge rate. In this work, the total current i_{total} is 4.8066.10⁻¹⁵ A. The surface integration of current density over the LFP/collector boundary is equal to i_{total} :

$$i_{total} = \oint_{nc} n_{ns} \cdot i_s \tag{2}$$

where i_s the current density vector, n_{ns} is the normal vector of the contact boundary pointing into the LFP electrode. Assuming that the current distributed uniformly on the collector, the discharge current density could be obtained from equation:

$$J = \frac{i_{total}}{\pi \cdot r^2} \tag{3}$$

The roughly estimated current density J for HCC and SCC are 382.5 and 2.44 A m⁻².

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.09.049.

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