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Letter to the editor

Efficient conducting networks constructed from ultra-low concentration carbon nanotube suspension for Li ion battery cathodes

A B S T R A C T

Carbon nanotubes (CNTs) with large length-diameter ratios and high conductivity are ideal to fabricate conductive networks in cathodes for Li ion batteries. However, good dispersion of CNTs in cathodes remains great challenge. Here, a CNT suspension containing an ultra-low concentration (0.2 wt%) of vertically-aligned CNTs (VACNTs) is used to construct a well-dispersed conductive network in cathodes. The VACNTs exhibit excellent dispersion stability in N-methyl pyrrolidone due to less entangling between CNTs. Significant promotion in specific capacities and low temperature performance have been achieved by adding highly-dispersed VACNTs into $LiFePO_4$ cathodes.

Lithium ion batteries (LIBs) are widely used in our daily life. For better performance of electrically-driven mobile devices, further promotion in the energy density of LIBs is highly desired. Cathode materials for LIBs usually exhibit low electric conductivities, such as ~10^{-9} S/cm for $LiFePO_4$ (LFP), ~10^{-4} S/cm for $LiCoO_2$ (LCO) and ~10^{-6} S/cm for $LiMn_2O_4$ (LMO) [1]. Therefore, constructing a conductive network in cathodes is crucial to enhance the rate performance and avoid battery failure [2]. Carbon black (CB) or acetylene black with sphere morphology is a widely-used conductive additive because of its high conductivity and good dispersibility [3]. The additive amount of CB in a cathode is usually as high as 4–10 wt%, for constructing a conductive network. Although more conductive path ways are formed at a higher CB addition in a cathode, ion blockage might be aroused due to the surface area coating by CB and binder and the consequent reduction of electrolyte transport pathway [4]. Loss of contact between CB particles due to the volume expansion and contraction of cathodes might lead to battery failure. Carbon nanotubes (CNTs) with a length-diameter ratio higher than 1000 are ideal materials to fabricate conductive networks in cathodes [5]. By using the CNT-NMP (N-methyl pyrrolidone) slurry as a conductive additive, the addition of CNTs can be reduced to 2–3 wt%. However, in the mass production of CNTs using fluidized beds [6,7], curled CNTs are produced in the form of agglomerates. As the result, stubborn agglomerates of CNTs is often observed in the CNT-NMP slurry, and good dispersion of CNTs in cathodes still remains great challenge.

Here, less-entangled vertically-aligned CNTs (VACNTs) are employed to construct a conductive network in cathodes. Stable dispersion of the VACNTs in NMP is achieved at an ultra-low concentration (0.2 wt%) of the nanotubes, and the as-obtained suspension is used in the preparation of cathode slurry. The addition of a small amount of VACNTs has efficiently established conductive networks and markedly promoted the charge-discharge capacities and low temperature performance for LFP cathodes.

Fig. 1a shows a theoretical model for the CNT conductive network in a LFP cathode. Each LFP particle in the model contacts with 3 CNTs in x, y and z orientations. To calculate the volume for LFP and CNTs in the model, the LFP particle size and the CNT diameter are determined based on the transmission electron microscopy (TEM) observation of typical samples. The particle size of a typical LFP sample is around 0.1–0.4 μm (Fig. 1b). The typical outer and inner diameter for CNTs is ~15 and 5 nm (Fig. 1c). The real densities for LFP and CNTs are 3.6 and 2.2 g/mL. The CNT proportion in the LFP-CNT assembly is calculated using the volume and density data. Fig. 1d shows the theoretical CNT proportions at different LFP particle size. A CNT concentration of only 0.75 wt% is needed for 0.2 μm LFP particles, and 0.12 wt% for 0.5 μm particles. The analysis of the theoretical model indicates that a CNT additive amount much less than 2–3 wt% is enough to construct a perfect conductive network if an ideal dispersion of CNTs is achieved, which ticks us to further explore the low-concentration CNT addition in LIB cathodes.

In a CNT-NMP suspension, CNTs are easier to entangle with each other at a high concentration, and better dispersion of CNTs is promising to be obtained at a low CNT concentration. Therefore, CNT-NMP suspensions with a CNT concentration of 0.2 wt% were prepared in order to achieve better dispersion of CNTs. Two CNT samples were prepared: agglomerated CNTs (ACNTs) prepared using a $FeMo/Al_2O_3$ catalyst in a fluidized bed [8,9], and VACNTs prepared using a ferrocene-cyclohexance solution as catalyst and carbon source [10,11] (see Supporting Information for experimental details). As shown in Fig. 2a, obvious agglomerates are observed in ultrasonically-dispersed ACNTs. Although a uniform suspension containing 0.2 wt% ACNTs had been obtained after ultrasonification, obvious precipitation of CNTs was observed after 48 h. It indicates that the 0.2 wt% ACNT suspension is not stable, probably due to the

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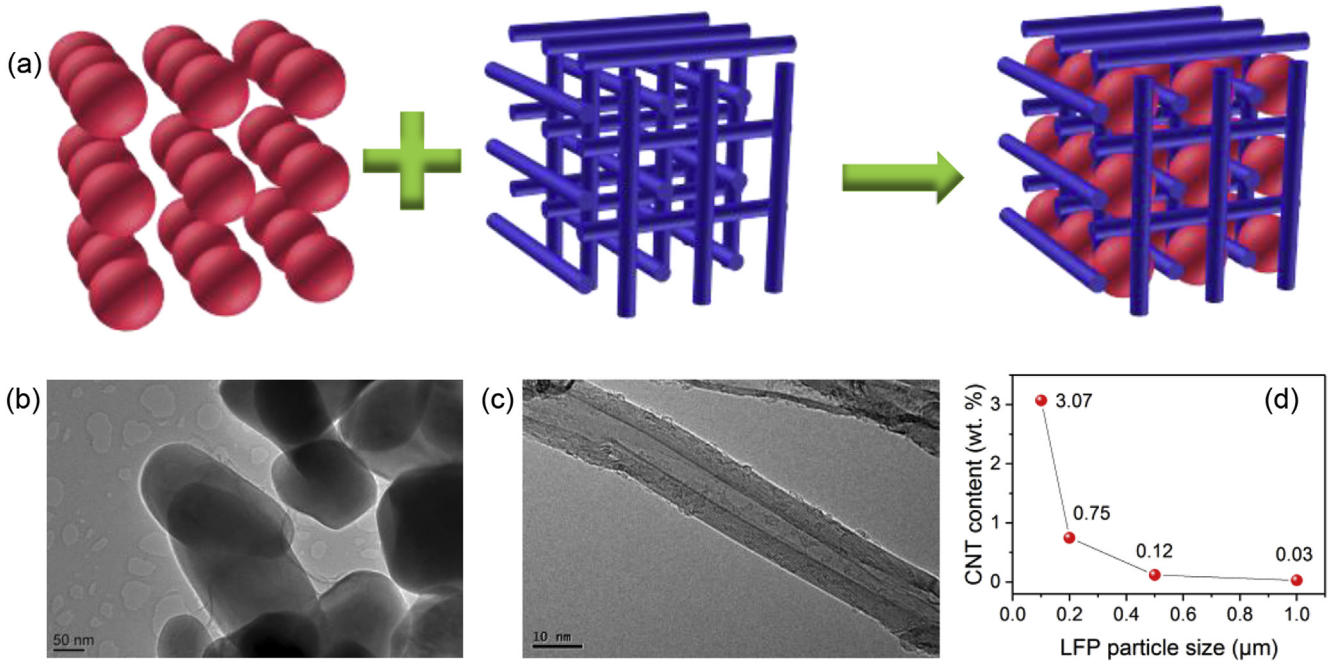

Fig. 1. (a) Model of a 3D CNT conductive network in LIB electrodes. The spheres represent cathode particles, and the cylinders represent CNTs. Typical TEM images of LFP (b) and CNTs (c). (d) The CNT content in the model at different LFP particle size.

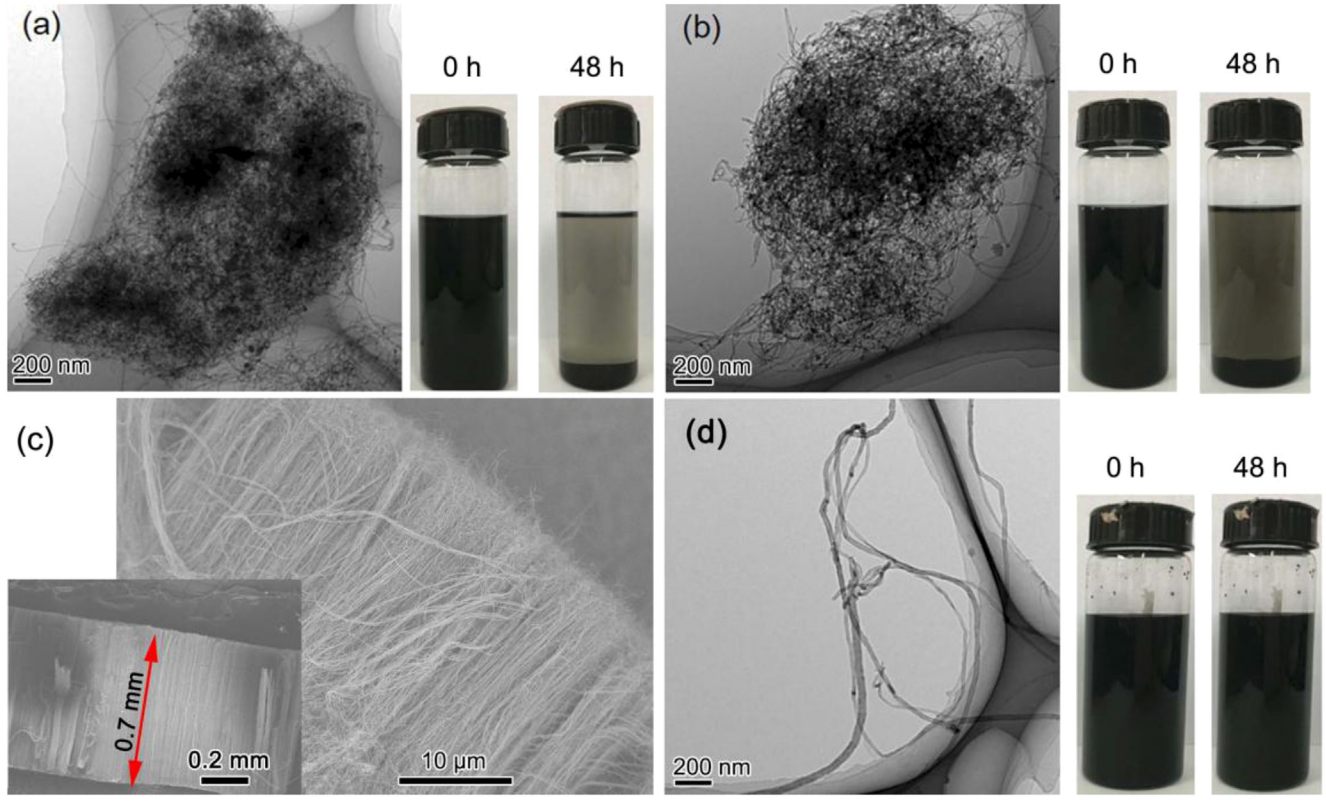

Fig. 2. TEM images and photos of the 0.2 wt% CNT-NMP suspensions for ACNTs (a), ball-milled ACNTs (b) and VACNTs (d). (c) Scanning electron microscopy (SEM) images of VACNTs.

agglomeration of ACNTs. Some stubborn agglomerates in ACNTs still exist after applying ball milling for 60 min to ACNTs (Fig. 2b). In contrast, no agglomeration or entangling of nanotubes is observed in the VACNTs (Fig. 2c), and individual CNTs are often observed in a wide TEM view field (Fig. 2d left). As the result, the 0.2 wt% VACNT suspension exhibits excellent stability even after still standing for 48 h (Fig. 2d). The height of the VACNT array is ~0.7 mm (the inset of Fig. 2c), and the diameter of the VACNTs is