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Surface-engineering of layered $LiNi_{0.815}Co_{0.15}Al_{0.035}O_2$ cathode material for high-energy and stable Li-ion batteries

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ABSTRACT

Surface engineering is an effective strategy to restrain the generation of rocksalt NiO phase on surface of layered $LiNi_{0.815}Co_{0.15}Al_{0.035}O_2$ (NCA) primary nanoparticles, a representative Ni-rich layered oxides cathode materials. Herein, we demonstrate the kilogram-scale synthesis of few-layer reduced graphene oxide (rGO) conformably coated NCA primary nanoparticles cathode materials by a mechanical wet ball-milling strategy. The lightening rGO coating layer effectively avoids the direct contact of electrolyte and NCA with rapid electrons transfer. As a result, the as-obtained NCA@rGO hybrids with only 1.0 wt% rGO content can deliver a high specific capacity (196 mAh g^{-1} at 0.2 C) and fast charge/discharge capability (127 mAh g^{-1} at 5 C), which is much higher than the corresponding NCA nanoparticles (95 mAh g^{-1} at 5 C). Even after 100 cycles at 1 C, 91.7% of initial reversible capacity is still maintained. Furthermore, a prismatic pouch cell (240 mAh) is also successfully assembled with the commercial graphite anode.

1. Introduction

The development of high-energy density and stable lithium-ion batteries (LIBs) is imperative to meet the ever-increasing requirement of portable electric devices and electric vehicles (EVs) [1–5]. The cathode materials, as the key component of LIBs [6], seriously restrain their energy density because of the low actual specific capacity. For example, the popular and widely applied $LiCoO_2$ cathode materials only deliver a specific capacity of 140 mAh g^{-1} in practical applications [7]. Moreover, metal cobalt is toxic and expensive [8]. Recently, layered Ni-rich $LiNi_{0.815}Co_{0.15}Al_{0.035}O_2$ (NCA) ternary cathode materials have attracted much attention on account of their desirable actual specific capacity as high as 180 mAh g^{-1}, high potential (vs. Li/Li^+) and greatly reducing the metal cobalt content [9–11]. However, the inactive NiO phase with rocksalt structure is easily grown on the surface of NCA nanoparticles during the repeated charge/discharge process, and hence resulting in the rapid capacity loss [12–16].

Surface engineering is a prevalent strategy to address the aforementioned issues of NCA, e.g., surface coating of metal fluoride (AlF_3) [15], metal oxide (Al_2O_3, MgO, ZnO) [17,18], metal phosphates ($AlPO_4$, $CoPO_4$) [19,20]. The introduction of such surface passivation layer will effectively impede the direct contact between NCA and electrolyte, giving rise to the enhanced cycling stability. Notably, they are electrochemically inactive with high density, which will inevitably sacrifice partial gravimetric specific capacity [21,22]. Furthermore, the electrons/ions transfer will be also blocked by these low conductivity coating layers, resulting in poor rate capability [19,21]. In recent years, graphene has been extensively applied to modify cathode materials because of its very low density (1.06 g cm^{-3}) [23] and excellent conductivity. For instance, Hersam et al. reported graphene-modified $LiMn_2O_4$ cathode, where PMMA/graphene films were obtained by growing graphene on Cu foil using CVD method, spin-coating PMMA on the top of graphene/Cu foil and the following Cu etching. And then, the cathode was manufactured by transferring the as-obtained PMMA/graphene film onto the $LiMn_2O_4$/steel substrate, which can maintain 90% of initial reversible specific capacity even after 750 cycles [24]. However, such technology involves sophisticated and complicated preparation process. Therefore, it is great challenging to exploit a facile and scalable strategy to fabricate graphene-modified cathode materials.

Herein, we demonstrate the scalable synthesis of few-layer reduced graphene oxide (rGO) coated NCA cathode materials (labeled as NCA@rGO) on kilogram level by a mechanical wet ball-milling strategy, in which GO has been in-situ thermally reduced and conformably covered on the surface of NCA primary nanoparticles. The lightening rGO coating layer can not only effectively suppress

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the generation of rocksalt NiO phase of the NCA nanoparticles, but also significantly accelerate the electrons transfer, leading to rapid charge/discharge capability and excellent cycling stability. As a result, the NCA@rGO hybrids with only 1.0 wt% rGO content can greatly enhance the specific capacity of pure NCA by 32.3% (195.9 mAh g^{-1} at 0.2 C) and 33.7% (127.3 mAh g^{-1} at 5 C). Even after 100 cycles at 1C, 91.7% of initial reversible capacity is still maintained. Furthermore, a prismatic pouch cell (240 mAh) is also successfully assembled with the commercial graphite anode.

2. Experimental

2.1. Synthesis of the NCA@rGO nanoparticles

A modified Hummers method was applied to prepare graphene oxide (GO) powders [25–28]. The NCA@rGO nanoparticles were synthesized by a mechanical wet ball-milling the mixture of GO suspension (1 wt%) and commercial NCA microparticles (BTR in Shen Zhen of China) for a few minutes. About 0.1 kg of the powder can be obtained for each time. For comparison, the corresponding pure NCA nanoparticles were also synthesized by the similar approach just without the addition of GO.

2.2. Characterizations

X-ray diffraction (XRD; Rigaku D/Max2550, Cu $K\alpha$ radiation) was employed to identify the crystalline phases of as-obtained samples at a scan rate of 1° min^{-1}. The structure and morphology of all powders were characterized by field-emission scanning electron microscopy (FESEM; Hitachi, S-4800) and transmission electron microscopy (TEM; JEOL, JEM-2100F) operated at 200 kV with an X-ray energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS; AXIS Ultra DLD, Al $K\alpha$ X-ray source) spectra were obtained with a magnesium anode to detect types of oxygen functional groups. All XPS data were calibrated using the C 1*s* peak at 284.8 eV as an internal standard. Raman spectra were recorded with NEXUS 670 FT-IR Raman spectrometer.

2.3. Li-ion battery assembly and electrochemical characterization

The positive electrodes were prepared by mixing the active materials, carbon black (Super-P) and polyvinylidene fluoride (PVDF) at a mass ratio of 8:1:1 in N-methyl pyrrolidone (NMP) solvent to form high-quality slurry, which was then coated on a pure aluminum foil. The typical loading mass is about 1.5 mg cm^{-2}. The coin-type 2016 half-cells are assembled in an argon-filled glove box with a pure lithium foil as the negative electrode, which were separated by a polypropylene membrane (Celgard 2400) soaked in electrolyte consisting of 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1:1 in volume). The prismatic pouch cells were assembled by many semi-automatic machines. For NCA@rGO cathode, after double coating the high-quality slurry on an aluminum foil, we cut the foil into identical narrower strips. The graphite anode is prepared by the similar approach just using a copper foil. To make the core of a pouch cell, we stacked the cathode and anode electrodes which were separated by the same membrane. After welding the pole ears, the core was packed and soaked in the same electrolyte in an argon-filled glove box. Finally, we acquired a prismatic pouch cell with stable performance after the per-charge and debubbling processes. The charge and discharge performances were observed by a LAND-CT2001C test system within a potential window of 2.75–4.3 V at different current densities. Electrochemical impedance spectra (EIS) were analyzed by an Autolab PGSTAT302N electrochemical workstation in the frequency range of 100 kHz to 0.01 Hz under constant voltage mode. Cyclic voltammetry curves were carried out on PGSTAT302N workstation within potential range of 2.75–4.3 V at a scan rate of 0.2 mV s^{-1}.

3. Results and discussion

3.1. Material design and structure characterization

Fig. 1 schematically illustrates the facile preparation of the NCA@rGO hybrids. Typically, the mixture of GO suspension and the commercial NCA microparticles (denoted as NCA MPs) (Fig. S1a) was ball-milled for a few minutes at room temperature, in which few-layered rGO nanosheets conformably covered on the surface of NCA primary nanoparticles. After drying, the NCA@rGO hybrids were obtained in kilogram scale. For comparison, we also synthesized the corresponding pure NCA nanoparticles (Fig. S1b) just without the addition of GO suspension. Fig. 2(a) shows the X-ray diffraction (XRD) profiles of the two samples. All the diffraction peaks are indexed to the α-$NaFeO_2$ layered structure [11,29], which is in good agreement with the analysis of the commercial NCA MPs (Fig. S2). This result reveals the well-maintained crystal structure of NCA after a ball-milling process, in which graphene oxides are in-situ thermally reduced. To certify it, first, the C 1*s* X-ray photoelectron spectroscopy (XPS) (Fig. 2b) was performed to study the oxygen functional groups on the graphene structure of NCA@rGO hybrids. Compared with that of pure GO (Fig. S3a), the C 1*s* XPS of NCA@rGO only consists of the evident peaks at 284.6 eV (C=C) and 285.2 eV (C–O), which indicates that the peaks of 286.9 eV (C=O) and 288.5 eV (O=C–O) disappear after a ball-milling process, demonstrating that some oxygen functional groups are reduced [30]. Second, the Raman spectrum of NCA@rGO hybrids is exhibited in Fig. S3(b) with an increasing intensity ratio of D band to G band (I_D/I_G), which further indicates graphene oxides are reduced during ball milling process [31,32]. Moreover, the increasing I_D/I_G also implies that more defects are grown in the graphene structure [33,34], which creates rich Li^+ insertion active sites and then accelerates the ions transfer. Fig. 2(c) shows the field emission scanning electron microscopy (FE-SEM) image of NCA@rGO hybrids. It is clear that the rGO layer homogeneously covers on the surface of NCA primary nanoparticles with sizes from 300 to 700 nm. For regulating the thickness of rGO layer, we also synthesized modified NCA cathode with different GO contents, as shown in Fig. S4. From Fig. 2(d), the high-magnification and high-resolution TEM images (inset) further present the homogeneous rGO coating layer with thickness of ~3.9 nm. Moreover, the HRTEM also demonstrates the NCA crystalline structure, indicating the interplanar distance of 0.25 nm which is corresponding to the (1 0 1) plane of NCA. We further detected the elemental distributions of the as-milled NCA@rGO ternary cathode. In Fig. 2(e–i), all of Ni, Co, Al and C elements are almost overlapped along with the NCA nanoparticles, which demonstrates the successful synthesis of NCA@rGO hybrids. Importantly, few-layered rGO coating layer can not only effectively suppress the phase transition, but also obviously accelerates the ions transfer, giving rise to remarkably improved electrochemical performances.

3.2. Electrochemical performance

We detected the electrochemical performances of the samples by assembling them into 2016 coin-type half-cells. As depicted in Fig. 3(a), the initial 3 cyclic voltammetry (CV) curves of NCA@rGO hybrids were measured at 0.2 mV s^{-1} within potential range of 2.75–4.3 V. According to Fig. 3(a), there are three couple peaks located at 3.75/3.66, 4.01/3.95, 4.20/4.15 V vs. Li/Li^+, respectively. They are corresponding to the three phase transition processes: H1 (hexagonal phase) → M (monoclinic phase), M (the monoclinic