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Enabling high rate charge and discharge capability, low internal resistance, and excellent cycleability for Li-ion batteries utilizing graphene additives

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ABSTRACT

A liquid-phase mixing method is adopted to uniformly disperse the graphene nanosheets onto $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode for high-performance Li-ion batteries (LIBs). The electrochemical performance was characterized using a full pouch cells with state-of-the-art electrode areal loading (compared to half coin cells). The addition of graphene sheets (i.e., only 1 wt%) significantly improves the high rate capability for charging and discharging operation. For example, 6 times improvement in 5 *C* charging was achieved providing further insights in enabling extreme fast charging for LIBs. Other benefits include longer cycleability, lower internal resistance, and higher lithium ion diffusion coefficient, demonstrated by charge-discharge cycling tests and electrochemical impedance spectroscopy. Higher capacity retention of 88.2% and decreased internal resistance of ~0.9 Ω are observed after 400 cycles. The diffusion coefficient of Li ions is $6.49 \times 10^{-8}\ cm^2\ s^{-1}$ when charged to 4.2 V, which is approximately 1.37 times higher compared to the configuration with no graphene sheet ($4.74 \times 10^{-8}\ cm^2\ s^{-1}$). The improved performance is ascribed to a robust network among the active materials formed by graphene sheets, which serves as an extended current conductor and facilitates charge transfer, ionic reversibility, and ionic transportation.

1. Introduction

Design and engineering high performance energy storage devices is one of the great challenges facing various types of applications [1]. To meet such a substantial energy storage demand for portable electronics, stationary devices and electric vehicles, the Li-ion battery technology offers an excellent reversible energy storage solution thanks to intrinsic high energy and power densities [2,3]. It is generally recognized that the energy and power densities of Li-ion battery strongly depend on the electrochemical performance of electrode materials. Particularly, engineering the cathode electrode is of a great importance. Therefore, the selection of cathode material is a crucial factor greatly influencing the specific capacity, safety, cycle life and overall cost. Ternary $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (LNCM) is a promising cathode material that integrates the benefits of $LiNiO_2$, $LiMnO_2$ and $LiCoO_2$ and provides high specific capacity, superior thermal stability, and lower cost [4–9]. However, LNCM cathode still suffers from low electronic conductivity, high reactivity between delithiated cathode and electrolyte, and serious dissolution of transition metal ions and electrolyte [10]. Therefore, significant work is required to improve the performance of LNCM cathodes. One of the promising strategies for improving the performance is to coat an optimal carbon layer onto the surface of LNCM cathode. The addition of such a coating layer not only protects the dissolution of transition metals but also assists Li^+ diffusion in the solid solution and electron jumping across the electrode [5].

Graphene nanosheet (GN) is a free-standing two-dimensional crystal with individual atomic-layer or serval layers, comprising sp^2-bonded carbon structure [11]. The extraordinary electronic properties such as mobility of charge carriers (~200 $k\ cm^2\ V^{-1}\ s^{-1}$) [12] and excellent thermal conductivity (~5 $kW\ m^{-1}\ K^{-1}$ for single-layer GN) [13] enable GNs as a promising electron conducting

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additive for both electrodes of Li-ion batteries. Recently, tremendous efforts have been made to improve the electrochemical performance using GN for lithium iron phosphate ($LiFePO_4$, LFP) cathodes. The preparation methods for GN-LFP composite cathodes include physical mixing [14], self-assembly [15], spray drying followed by post annealing [16], and simultaneous *in-situ* formation of LFP and GNs [17]. The as-prepared GN-LFP cathodes have been demonstrated to exhibit superior rate capability. The enhanced performance is due to the GNs' unique capability in creating more effective three-dimensional conductive network in the LFP cathodes [1,18–20], compared to conventional carbon additives such as carbon black. This unique finding suggests the development of novel techniques for the preparation of GN-LNCM cathodes for further improving the electrochemical performance and engineering the cathode structure of Li-ion batteries.

Several methods including mechanical mixing [21] and micro emulsion/ball milling [22] have been employed to fabricate GN-LNCM composite cathodes, showing high reversible capacity and excellent rate capability. However, these electrochemical systems are only operational in half coin cells, which is not beneficial for practical applications. Accordingly, the main objective of this work is to explore an efficient liquid-phase mixing method to prepare well-dispersed GN onto LNCM cathode. The synthesized GN-LNCM composites, served as the cathode material, were electrochemically investigated in full pouch cells, using mesocarbon microbeads (MCMB) as the anode material. Electrochemical performance in the pouch cells including charge-discharge cycling and electrochemical impedance spectroscopy were systematically discussed. The procedure for electrode fabrication also provides a crucial pathway for assembling high-performance Li-ion battery pack using GNs as a conductive additive. The charging rate performance, usually being overlooked, is also investigated in the present work. The merit of this study focuses on (i) novel facile fabrication of GN-LNCM cathode, (ii) strategy to boost fast charging and (iii) superior performance of the cathode that offers excellent reversibility, high rate capability and enhanced cyclic performance, showing a commercial feasibility for practical applications.

2. Experimental

Commercial GN suspension used in this work was purchased and supplied from Cnano Technology Ltd. (Taiwan branch). The GN powders were prepared from the exfoliation of graphite powders, using a physical exfoliation method. The specification of GN products included: 3–5 nm in thickness and 10–15 graphene layers. The GN powders were uniformly dispersed in N-methyl pyrrolidinone (NMP) solvent to form the GN suspension through an efficient homogenization method.

Electrochemical performance was conducted within pouch cells using commercial LNCM and MCMB as cathode and anode materials, respectively. Herein both LNCM and MCMB powders were provided from Battery Energy Technology, Inc. (Taiwan). As for anode fabrication, the MCMB powders (average size: 25–30 μm) were mixed with a binder (poly-vinylidenefluoride (PVDF)) and a conducting medium (Super-P, Imerys Graphite & Carbon) in a weight ratio of 94.3:4:1.7 in NMP solvent to form the anode slurry. The mixture was blended by a three-dimensional mixer using Zr balls for 3 h to prepare uniform slurry. The resultant slurry was uniformly coated on a copper foil substrate with a doctor blade, followed by evaporating the solvent, NMP, with a blow dryer. The LNCM cathode consists of LNCM (95.4 wt%), GN (1.0 wt%), PVDF (2.4 wt%), and Super-P (1.2 wt%). To avoid GN aggregation, an efficient liquid-phase mixing method was adopted to prepare well-dispersed GN onto LNCM cathode. The GN suspension was uniformly distributed in PVDF/NMP solution, followed by dispersing of Super P and LNCM individually allowing the sequent dispersion of GN over the surface of LNCM powders. The mixing sequence is critical as it affects the homogeneity of electrode components and cell performance [23]. The cathode slurry was carefully pasted onto an Al foil, in which the coating process was very similar to the assembly of anode. For comparison, one LNCM cathode was also fabricated without adding GN powders. The compositions for both cathodes and the MCMB anode in this work are listed in the Supporting Information (see Table S1). As tabulated in Table S1, both LNCM and GN-LNCM cathodes had an identical dual mass loading (*ca.* 17.0 mg cm^{-2}) and apparent density (*ca.* 3.5 g cm^{-3}). The result revealed that the influence of GN additive on the physical properties of cathode is minor. It is important to note that the electrode loading is within the similar range to commercial batteries and thus, the results are much more representative for cell-level applications compared to small half coin cells, demonstrated in previous works [21,22].

To inspect the importance of adding sequence, this study adopted three types of adding sequence in the preparation of electrode slurries, as shown in Table S2. The other important parameter, GN amount, was used to clarify the influence of GN coating on the electrical conductivity of GN-LNCM cathodes. The chemical composition of each GN-LNCM cathode was collected and listed in Table S3. The electrical conductivity of cathode sheets was measured using a four-probe method. One thin-film probing system (KeithLink Technology Co., Ltd.) was employed to measure the electrical conductivity of as-prepared electrode sheets. The probe diameter and the probe spacing distance were approximately 100 μm and 1 μm, respectively. The electrical conductivity (σ_{avg}) was determined through averaging five readings measured at different locations of cathode sheet.

Both the cathode and anode sheets were dried at 135 °C in a vacuum oven for 12 h and then pressed under a pressure of about 200 kg cm^{-2}. The capacity ratio of anode to cathode was set *ca.* 1.2 for the design of pouch cells, and the sheet thickness was approximately 140 μm. The pouch cells were assembled in a glove box for the electrochemical characterization. The porous polypropylene film served as polymeric separator, and the electrolyte solution used here was 1.0 M $LiPF_6$ in a mixture of ethylene carbonate, polycarbonate, and dimethyl carbonate with a weight ratio of 1:1:1. The charge/discharge cycling test was performed at different *C* rates (varied from 0.5 to 5C) within the voltage range of 2.75–4.25 V at ambient temperature. Electrochemical impedance spectroscopy (EIS, CH Instruments 608C) was employed to assess the electrochemical behavior of as-prepared Li-ion batteries upon conducting various cycling experiments. The EIS measurement was carried out at open-circuit potential with the frequency range of 100 k–0.01 Hz. The microstructures of GN-LNCM composites were characterized by a scanning electron microscope (SEM, JEOL JSM-5600) and a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100).

3. Results and discussion

The HR-TEM photograph, as shown in Fig. 1, reveals that the transparent GNs consist of several stacked graphene layers. The images demonstrate that natural graphite powders have been physically exfoliated by the mechanical exfoliation method, followed by a sequent ultrasonic dispersion treatment. The cross-sectional views indicate that the number of graphene layers is in the range of 10–15. Fig. 2(a) shows the optical microscopy images of GN-LNCM cathode sheets before (upper) and after (lower) calendering. It can be seen that the GNs were uniformly dispersed over the LNCM powders since there are no visible GN aggregates onto the surface of cathode sheets. To determine optical parameters