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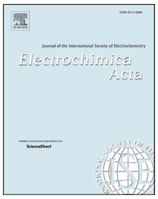

Influences of different reaction mediums on the properties of high-voltage $LiNiPO_4$@C cathode material in terms of dielectric heating efficiency

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Nanoscale, $LiNiPO_4$-core and carbon-shell high voltage (>5 V) $LiNiPO_4$@C cathode materials have been synthesized using a microwave & solvothermal methodology using different solvents, ethylene glycol, isopropanol, isobutanol and water as the reaction medium. The effects of these solvents on the crystal-quality, morphology and electrochemical qualification of the produced materials have been evaluated in terms of the heating efficiency in the microwave field by using various opto-analytical techniques and electrochemical measurements. The heating characteristics in terms of the absorption of the energy as part of the microwave-material interaction phenomenon is also discussed. X-ray diffraction analyses demonstrate that it is possible to synthesize substantially pure $LiNiPO_4$ crystal using isopropanol as the reaction medium. High-resolution transmission electron microscopy analysis reveals that this combined methodology can provide core-shell morphology with a 5–6 nm coating thickness. The $LiNiPO_4$@C cathode material produced in an isopropanol environment exhibits the best electrochemical properties, achieving a discharge capacity of 157 mAh g^{-1} at a 0.1 C-rate, and shows almost 81% capacity retention at the end of the 80th cycle. Thus, this paper offers a perspective for solving the difficulties encountered in modifying a high voltage $LiNiPO_4$ cathode, especially the deficiency in terms of cycle life behavior, and the further benefits are highlighted.

1. Introduction

Today, the need for high-performance lithium-ion batteries from reaching the cathode materials currently used to be replaced by operating with a higher redox potential is a desirable development. $LiNiPO_4$ cathode material has the highest operating voltage of all the phospho-olivine cathode materials, with an active redox potential of 5.1 V vs. Li/Li^+, and a theoretical specific energy density of about 800 Wh kg^{-1} [1]. These electrochemical performances are superior to those of comparable energy density isostructural $LiFePO_4$ cathodes with approximately 580 Wh kg^{-1} which are commercially available in applications such as hybrid and/or full electric vehicles [2] and can produce 3.45 V vs. Li/Li^+ [3]. However, the successful implementation of a $LiNiPO_4$ cathode cannot be achieved due to the low electronic and ionic conductivities, and the limited oxidative stability of conventional electrolytic solutions [4–6]. In addition to the ion doping [6,7] and conductive coatings [8,9] used to solve the above-mentioned drawbacks, synthetic methods have been tried using morphology control in order to improve the diffusion abilities and to reduce the particle size [10]. In these synthetic routes, soft-chemical synthesis methods such as the sol-gel [6,11,12], hydrothermal/solvothermal [13–16] and polyol methods [17] allow for kinetic control and are used extensively because of their proven effectiveness. However, many of these approaches are combined with high temperature annealing and carbon coating to ensure that the material has a good crystalline structure and sufficient electronic conductivity [18–20].

At this point, detailed engineering applications and surface modification studies are required to improve the unstable nature of the $LiNiPO_4$ cathode material. The widespread use of advanced materials in energy storage research makes the need for efficient, time-saving and environmentally friendly manufacturing processes more important by overcoming the difficulties of processing these functional materials. The microwave material processing technique offers a unique solution in the framework described above. Complex heating characteristics in the synthesis processing of materials have a significant effect on their conversion to functional products

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[21]. Heat directly affects atoms and/or molecules, and creates a temperature gradient along the material, having a dominant effect on the microstructural and mechanical properties of the material [22]. In practice, most production methods used to synthesize advanced electrode materials include intense interaction with heat, so the thermal energy based on conventional route, is closely connected to effective heat transfer between the source and the target material. Thus, the inadequacy of traditional thermal methods is a reason for the development of new techniques for synthesizing efficient and versatile materials. Another important issue is the behavior and structural properties of solvent molecules used as reaction environment in the microwave field. During synthesis, the solvent functions as a reaction medium, and can play crucial roles due to its physicochemical properties. Firstly, it provides the ability to control the chemical reagent concentration that affects the reaction kinetics, and generally increases the solubility and reactivity of the compounds under high temperature and pressure. Secondly, the solvents can modulate the growth of crystals that induce specific structures, providing coordination between the dissolved species in the reaction environment. Thirdly, in a microwave & solvothermal synthesis, one of the most crucial properties is the polarity of the solvent, in that the greater the polarity of the reaction mixture, the greater the ability to interact with microwave energy, and the more effective heating can be achieved. Solvents have also been found to play an important role in controlling the morphology and particle size of cathode-active materials, as well as their crystal structure. Ludwig et al. [23] have shown a clear relationship between the particle size and electrochemical properties of the solvent species and the composition of the high-voltage $LiCoPO_4$ cathode material. In this mentioned work, $LiCoPO_4$ products obtained using a microwave-assisted solvothermal process, and using high ethylene glycol percent solvent as a medium, exhibit the highest capacity, gravimetric energy density and excellent cycle performance. In another study, Makarova et al. [24] proved a correlation between the dielectric constant of the solvent and the synthesis of potassium tantalite structures. In low permeability solvents, the pure cubic perovskite $KTaO_3$ structure is formed, whereas the increase in permeability triggers pyrochlore $K_2Ta_2O_6$ formation or phase mixture formation. In similar studies, the effects of solvent selection on the crystal structure and morphological properties of the material produced were evaluated [25–27].

Recently, our group reported an exceptional microwave synthesis derivation technique for the synthesis of $LiCoPO_4$ and $LiNiPO_4$ cathode materials separately [28–30], entitled low-level and long-time microwave and solvothermal synthesis (LLLTMSS), in which high crystal quality cathodes and highly qualified electrochemical properties were obtained. This approach refers to delivering microwave energy emitted on particles rather than sending it in a short time, spreading the same amount of energy over the prolonged time period. However, as is well known, the ongoing problems such as low crystal quality and lack of cyclic stability of these two high-voltage cathode materials have not yet been solved, and it seems unlikely that progress in the current situation will follow the development processes of the $LiFePO_4$ cathode. Therefore, the progress made on the subject is of great importance, and some leading edge published works on the synthesis of high voltage olivine phosphate cathodes by microwave and/or solvothermal methods are summarized in Table 1. The effects of the newly-elaborated synthesis methodology and the perfect core-shell morphology so produced on the electrochemical features are concentrated in terms of rate capability and cycle stability. The advantages of this microwave application, which includes acceptable reaction times and more homogeneous reaction conditions with lower temperature gradients, and the promising results, have led to the formation of the desired core-shell particles and have triggered further investigation of this approach. In this current work, the effects of four solvents selected from different segments (Polarity, dielectric constant, heating efficiency, ect.) on the structural, morphological and electrochemical properties of $LiNiPO_4$ cathode material in terms of dipol moments and heating efficiencies (tan δ) were investigated and discussed. Thus, we draw the reader's attention to an effective approach to solving the fundamental problems associated with 5.1 V $LiNiPO_4$ cathode material.

2. Experimental procedure

2.1. Synthesis

$LiNiPO_4$ core and carbon shell cathode materials were prepared by the LLLTMSS method. Ethylene glycol, isopropanol, isobutanol and water solvents were selected as the reaction environment for the heat conduction medium of microwaves during LLLTMSS methodology. Nickel (II) nitrate (Merck KGaA, Darmstadt, Germany) was used as a nickel source, lithium nitrate (Sigma-Aldrich, St. Louis, MO, USA) was used as a lithium source, and diammonium phosphate (Merck KGaA) was used as a phosphate source. As a carbon source, an alginic acid compound, which is distinguished by its ability to adhere to the surface, was used, and no further purification treatment was performed on the starting materials [39]. The precursors were dissolved in extra purified water with targeted rates. After the mixture reached a transparent form it was taken to a sealed solvothermal reactor (180 °C 20 Bar) under microwave irradiation (2.45 GHz, 600 rpm). A microwave process using an Anton Paar, Monowave Edu device was used for a total of 30 min, at a typical microwave power of 40–50 W.

Following these procedures the resulting solid was filtered and thoroughly dried overnight at 80 °C. Then, the resulting mixture was stirred with alginic acid (10% by weight) as the carbon supplier. The powders obtained from the use of four different solvents were mixed with purified water to ensure the formation of sufficient homogeneity by being sonicated for 120 min. The materials were then dried for a second time overnight and were calcined in a tube oven at 650 °C for 6 h under an argon atmosphere. In order to prevent agglomerating, the temperature change in the heating and cooling processes was applied at 0.5 °C per minute. The fine-grained black powder products obtained at the end of all these processes were from the derivative $LiNiPO_4$ olivine compound.

2.2. Characterization

The core-shell $LiNiPO_4@C$ cathode materials were structurally, morphologically and electrochemically analyzed. The synthesized powders were recorded by X-ray powder diffraction on a Panalytical Empyrean X-ray diffraction device using Cu Kα radiation ($\lambda = 1.5406$ Å) in the range of 15–55°. As a secondary structural characterization, fourier transform infrared spectroscopy analyses of samples were conducted using a Perkinelmer Frontier spectrometer device. The surface morphology of the synthesized samples was recorded by a field emission scanning electron microscope using a Hitachi SU8010 device. High-resolution transmission electron microscope images were collected using a Jeol 2010F TEM operating at 200 keV. The cell volumes and lattice parameters were determined by Rietveld analysis using the MAUD (versiyon 2.74) software.

The charge-discharge tests were carried out on an Origalys Origaflex potentiostat/galvanostat/impedance meter system, between a constant rate of 0.1–5 C, 1 C = 167 mA h g^{-1} [8]. The potentiometric measurements were performed at an ambient

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