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Improved electrochemical and thermal properties of nickel rich $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode materials by SiO_2 coating

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HIGHLIGHTS

- Nano-sized SiO_2 was uniformly coated on the surface of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode.
- Thermal stability and cycle performance are improved by SiO_2 coating.
- EIS results suggest that side reaction on interface is suppressed by SiO_2 coating.
- SiO_2 coating shows significant HF scavenging effect.

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ABSTRACT

A surface coating of SiO_2 is applied to a Ni rich $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material in a bid to improve its electrochemical and thermal properties. A uniform coating is achieved through a wet process using nano-sized SiO_2 powder, and though the coated electrode is found to exhibit a reduced rate capability, its cycle performance at a high temperature of 60 °C is greatly enhanced. The effect of this SiO_2 coating is further investigated by electrochemical impedance spectroscopy, which confirms that it suppresses the growth of interfacial impedance during progressive cycles. The SiO_2 coating also demonstrates good HF scavenging ability, producing a subsequent reduction in the degradation of the active core material. The thermal properties of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ are also improved by the SiO_2 coating due to a reduction in the direct contact between the electrode and electrolyte. On the basis of these results, SiO_2 coating is considered a viable surface modification method for improving the electrochemical and thermal properties of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$.

1. Introduction

Over recent years, the range of lithium ion battery applications has increased from small mobile devices to larger-scale uses such as electric vehicles (xEVs: HEVs, PHEVs and EVs) and energy storage systems (ESSs). This, in turn, has driven demand for lithium ion battery systems that can offer a higher energy density, faster charge, greater safety and lower cost [1,2]. These are all critical factors in ensuring the commercial success of EVs, with driving distance (i.e., high capacity and working voltage) being of particular importance. With this in mind, Ni rich layered $LiNi_xCo_yMn_zO_2$ (NCM, where $x > 0.5$, $x + y + z = 1$) and Li rich layered composites ($1\text{-}xLiMeO_2\text{-}xLi_2MnO_3$) are considered amongst the most promising cathode materials for use in EVs [3–10]. This is especially true of Ni rich layered $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622), as its high proportion of Ni in transition metal sites ensures a high capacity [6,7,11]; however, this increase in Ni also creates an inherent structural instability that is well known in $LiNiO_2$ [12–14]. Such structural instability invariably leads to degradation in cell performance over time due to side reactions such as the dissolution of metal from the cathode into the electrolyte, as well as the formation of a solid electrolyte interface (SEI) on the cathode surface [14–16]. Furthermore, these undesirable reactions are greatly accelerated at elevated temperature (>60 °C), with the structural instability induced in fully-charged Ni rich cathodes being a

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notorious safety issue [17,18].

To overcome these problems, a metal oxide surface coating can be applied to the cathode to restrict its direct contact with the electrolyte and minimize the impact of side reactions [19]. For layered cathodes, there have been a number of oxides suggested as suitable coating materials, which has included: Al_2O_3, ZrO_2, TiO_2, SiO_2, $FePO_4$, $AlPO_4$, etc. [20–27]. From among these, SiO_2 has been selected as a coating material for NCM 622 in this study, as its particular thermal properties are anticipated to correlate with a good thermal stability. Moreover, SiO_2 provides a scavenging effect for the hydrogen fluoride (HF) that is commonly generated by a reaction between trace amounts of residual water in the electrolyte and $LiPF_6$ salt. This is an important benefit, as reaction between HF and the cathode surface typically causes degradation in performance during cycling [25,28–30]. In addition to this sacrificial protection, SiO_2 also offers the benefit of being a very low cost material. This study therefore explores the effect that a SiO_2 surface coating has on the electrochemical and physicochemical characteristics of a NCM622 cathode.

2. Experimental

Commercial-grade $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622, L&F materials) was used as both the base material for coating and as a pristine reference material. For surface coating, 0.5–3.0 wt.% of a nano-sized SiO_2 powder (average particle size < 10 nm, Aldrich) was first dispersed in 70 ml of isopropyl alcohol (IPA) by sonication for 20 min. To this was added 10 g of NCM622 powder, with the resulting solution then stirred at 60 °C for 6 h to evaporate the IPA. The resulting powder was then heated at 500 °C for 4 h under an air atmosphere to obtain SiO_2-coated NCM622.

Structural analysis was performed by X-ray diffraction (XRD) using an Empyrean diffractometer (PANalytical) equipped with a monochromated Cu Kα radiation ($\lambda = 1.54056$ Å). The morphology, microstructure, and composition of the prepared materials were examined using field-emission scanning electron microscopy (FESEM, JEOL JSM-7000F) and high resolution transmission electron microscopy (HRTEM, JEOL ARM-200F) with energy dispersive spectroscopy (EDS) mapping.

Working electrodes were prepared by coating Al foils with a slurry containing 95 wt.% active material, 2 wt.% carbon black (Super P) and 3 wt.% polyvinylidene fluoride (PVDF) dissolved in n-methyl-2-pyrrolidone (NMP). The electrodes were then pressed and dried for 12 h at 120 °C. Coin-type (CR2032) half-cells consisting of a working electrode, Li metal foil counter electrode, porous polyethylene membrane separator, and an electrolyte of 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:2 by volume) were subsequently assembled in a dry room with a controlled dew point of less than −45 °C. Using these cells, galvanostatic charge–discharge experiments were performed at a constant current of between 0.1 and 2C using a TOSCAT-3100U cycler (Toyo system Co.). AC-impedance measurement was carried out using a VSP-300 potentiostat/frequency response analyzer (BioLogic) with a three-electrode glass cell setup, wherein Li metal foil was used as the counter and reference electrode. The impedance spectra were measured within an applied frequency range of between 1 MHz and 10 mHz.

Differential scanning calorimetry (DSC, Model Star system, Mettler Toledo) was performed to investigate the thermal characteristics of the delithiated electrodes; the heating rate and temperature range were 5 °C min^{-1} and 25–400 °C, respectively.

3. Results and discussion

The XRD patterns showing the structural properties of pristine NCM622 powder (P-NCM) and NCM622 powders coated with 0.5, 1.0 or 3.0 wt.% SiO_2 (S-NCM) are given in Fig. 1. All patterns are in good accordance with a layered structure belonging to the R-3m (SG# 166) space group, with no evidence of any impurities within the detection limits of XRD. The absence of SiO_2 reflection is due to low amount of SiO_2 coating. No peak shifts is observed in the S-NCM, and the carefully refined lattice parameters indicate that there is no lattice expansion as a result of SiO_2 coating; the lattice parameters of P-NCM and S-NCM are $a = 2.867$ Å and $c = 14.218$ Å. Since the temperature used for coating (500 °C) is comparatively low with regards to the diffusion of Si, it is expected that the vast majority of the SiO_2 exists solely on the surface of NCM622.

The exact amounts of the SiO_2 coated on S-NCM were measured to be 0.53, 0.93 and 2.96 wt.% for S-NCM (0.5 wt.%), S-NCM (1.0 wt.%), and S-NCM (3.0 wt.%), respectively, by SEM-EDS analysis. The SEM images and EDS mapping results in Fig. 2 clearly show the SiO_2 coating of S-NCM, and that the degree of coating increases with the content of SiO_2. Meanwhile, the TEM images and STEM-EDS mapping results in Fig. 3 reveal that the thickness of SiO_2 coating is less than 10 nm. Given that the STEM-EDS mapping results also show that Si is highly concentrated at the surface of NCM622, we confirm that a uniform surface coating of nano-sized SiO_2 particles was successfully achieved.

Previous reports have mentioned that a fresh surface is revealed by heat treatment during coating [31,32], with Chen et al. also suggesting that the aged surface of cathode materials may be a contributing factor in capacity fading. Thus, the fresh surface that is exposed by washing or heating may enhance the electrochemical properties of the cathode material. To consider this effect, a P-NCM sample was washed in IPA solution, and then heated under the same conditions as those used for coating process so as to provide a fair evaluation of the electrochemical properties.

Fig. 4 illustrates the initial charge–discharge curves obtained at a rate of 0.1C. We see from this that the discharge capacity of P-NCM is 178.7 mAh g^{-1}, whereas that of the S-NCM is slightly lower and reduced to 175.7 mAh g^{-1} with an increase in the wt.% of the coating. Moreover, a slight overpotential is evident in the discharge curve of S-NCM, which is caused sluggish kinetics of Li^+ diffusion. This implies that the resistivity at the interface may be increased by a SiO_2 coating. The associated voltage drop is considered one of the main reasons for the low discharge capacity of S-NCM, although the reduced ratio of active material due to SiO_2 coating also plays a role.

To investigate the effect that a SiO_2 coating has on resistivity, the rate capability was determined at various C-rates, as shown in Fig. 5. It should be noted here that all discharge capacities were normalized with respect to the C-rate of electrode with the slowest rate at 0.1C. It is evident from this that 87.8% of the capacity of P-NCM at 0.1C is maintained up to about at 2C, whereas the equivalent capacity retention of S-NCM is 87.2% (0.5 wt.%), 81.7% (1.0 wt.%), and 64.5% (3.0 wt.%). This reduced rate capability for S-NCM can be explained by the fact that it is related to an interfacial reaction between the electrode and electrolyte, and since SiO_2 is a natural insulator, it is therefore no surprise that the electrical conductivity of the cathode material is reduced. Furthermore, the surface coating reduces the active surface area for Li^+ insertion, which also leads to a high resistance [33].

Fig. 6 shows the room temperature cycle performance at a constant rate of 0.5C, which reveals that the discharge capacity of P-NCM is 158.1 mAh g^{-1} after 50 cycles and its related capacity retention is 94%. For S-NCM, the discharge capacities are 159.5, 158.3, and 156.8 mAh g^{-1} for 0.5, 1.0 and 3.0 wt.%, respectively, with capacity retentions of 95, 95.4, and 97%. Although the cycle performance appears from this to be slightly improved in the case of S-NCM, it is difficult to conclusively prove that this directly attributable to the SiO_2 coating.