

Surface treatment of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material for lithium secondary batteries

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Abstract

The harmful side reactions between the cathode materials and liquid electrolyte within the lithium secondary batteries will deteriorate the performance of the cathode materials and batteries. The $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass with high Li^+ conductivity and stability can be coated on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders by mixing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, $\text{LiOH}\cdot\text{H}_2\text{O}$ and H_3BO_3 and heating the mixture at 500°C for 10 h. The structure of the surface-treated and base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders was characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET. It is shown the $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ layer can prevent $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ from contacting directly with liquid electrolyte, and minimize the side reactions within the batteries. The surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material has increased reversible capacity, decreased irreversible capacity, stabilized cycling performance, reduced self-discharge, especially the improved high temperature performance. The results indicated that the surface treatment should be an effective way to improve the comprehensive properties of the cathode materials for lithium secondary batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium secondary batteries; Cathode materials; $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$; Surface treatment; $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass

1. Introduction

The high voltage cathode materials that are being used in lithium secondary batteries are mainly the well-known LiCoO_2 , LiNiO_2 , LiMn_2O_4 and their derivatives [1]. In the batteries containing non-aqueous electrolyte, the cathode materials are contacting directly with the electrolyte. Some unwanted side reactions will occur at the interface, deteriorating the performance of the cathode materials and batteries [2].

Using the high voltage cathode materials, the cells must be charged up to voltages greater than 4 V so as to utilize their full capacity. At such high voltages, the electrolyte will be at the risk of being oxidized and decomposed. Fully charged, fairly delithiated positive electrode materials are strong oxidants, acting as catalytic agents toward electrolyte decomposition. The charged cathode materials are unstable because a large number of Li^+ -ions have deintercalated from their crystal lattice, resulting in the phase transformation, active materials decomposition and dissolution. The non-aqueous electrolyte will corrode the cathode materials and act as a catalytic agent toward charged cathode materials

deterioration. The harmful interactions between the cathode materials and electrolyte will create deleterious by-products, such as insulating passive film, gases, etc. The side reactions will cause the self-discharge, irreversible capacity, capacity degradation, and unsafety within the lithium secondary batteries, especially at elevated temperature.

In order to minimize the side reactions between the cathode materials and electrolyte, the surface of the cathode contacting with the liquid electrolyte must be reduced. Amatucci and coworkers [3,4] presented a surface treatment concept, in which a protective thin film was coated on the surface of the spinel LiMn_2O_4 . The physical barrier between the oxidizing spinel and the electrolyte can reduce the area of electrolyte/cathode interface, protect the electrolyte from the catalytic effects of the LiMn_2O_4 , and protect the LiMn_2O_4 from corrosion by the non-aqueous electrolyte. According to their reports, surface treatments are successful in improving the elevated temperature performance of spinel LiMn_2O_4 . They also pointed out that the use of surface treatments might offer advantages to the other intercalation compounds such as LiCoO_2 and LiNiO_2 which were also suffering from catalytic process with the electrolyte in the charged state at elevated temperature similar to those observed with spinel LiMn_2O_4 . However, the surface treatments of LiCoO_2 , LiNiO_2 and their derivatives are rarely reported.

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The layered $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material is considered as strong potential candidate to replace the actually commercialized LiCoO_2 because of its attractive advantages, such as lower cost and higher reversible capacity than LiCoO_2 , easier preparation and better cycling stability than LiNiO_2 , etc. [5]. Before $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ being put into practice, the material's comprehensive properties, especially at elevated temperature and charged state, should be further improved. It is expected that the surface treatment is an effective way.

According to the reports [3,4] of Amatucci and coworkers, lithium boron oxide (LBO) glasses are particularly suitable for surface treatment. There are several reasons. The first of these is that molten LBO compositions exhibit good wetting properties with respect to the ceramics. The combination of good wetting properties and relatively low viscosity in the molten state allow easy processing and result in even coverage with the use of a minimal amount of material. Secondly, LBO compositions have already been investigated as solid lithium ionic conductors which exhibit good ionic conductivity [6,7]. Furthermore, electrochemical studies have shown that these materials are stable against the high oxidation potentials of the 4 V positive electrode materials used in Li-ion batteries today. Finally, such materials have processing temperatures consistent with those of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

In this paper, the composition of the coating is chosen as $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass. The preparation, structure and electrochemical performance of the surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material have been discussed in comparison with the base one in detail.

2. Experimental

For the synthesis of base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders used throughout this study, $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Ni}(\text{OH})_2$, and $\text{Co}(\text{OH})_2$ were mixed in a stoichiometric ratio and heated to 750°C for 16 h in oxygen. The approach for applying coatings was to dissolve H_3BO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ ($\text{H}_3\text{BO}_3/\text{LiOH}\cdot\text{H}_2\text{O} = 2.0$, molar ratio) in methanol. The base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders were then added to the solution and the mixture was stirred and gently heated to $70-80^\circ\text{C}$ until the solvent was completely evaporated. The powders were then heated at 500°C for 10 h. The melting points of H_3BO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ are 186 and 445°C , respectively. Therefore, during heating the liquid H_3BO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ can wet the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, and H_3BO_3 reacted with $\text{LiOH}\cdot\text{H}_2\text{O}$ to produce LBO. After the mixture cooled to room temperature, the solid $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass was coated on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders. In this paper, the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders were coated with 1 wt.% of $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass.

The surface composition of the powders was characterized using X-ray photoelectron spectroscopy (XPS, VG, ESCALAB220i-XL). X-ray diffraction (XRD, Japan, D/Max-RB) using $\text{Cu K}\alpha$ radiation was used to identify the

crystalline phase and crystal lattice parameters of the powders. The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JSM6301F). The specific surface area of the powders was measured by the BET method with N_2 adsorption.

Experimental test cells for measurements used the cathode with the composition of 80 wt.% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 10 wt.% carbon black, and 10 wt.% PTFE. The separator was a Celguard 2400 microporous polyene membrane. The electrolyte was 1.0 M $\text{LiPF}_6\text{-EC} + \text{DEC}$ (1:1 by volume). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The charge-discharge cycling was galvanostatically performed at a current density of 0.5 mA cm^{-2} with cut-off voltages of 3.0–4.3 V (versus Li/Li^+) at 20 and 60°C , respectively.

3. Results and discussion

The surface composition of the base and surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders was determined by XPS. The results in Table 1 show the surface composition of the base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is very close to the stoichiometric ratio ($\text{Li}:\text{Ni}:\text{Co}:\text{O} = 25:20:5:50$, molar ratios). However, B and Li are enriched on the surface of the surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, although the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders were only coated with 1 wt.% of $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$, as indicated in Table 1. It follows that the $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ does not solute into $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, but coats on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders, as has been expected.

Fig. 1 shows the XRD spectra of the base and surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders. The spectra of the base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders indicates the material is single phase with order layered structure. The crystal lattice parameters of the base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ are $a = 2.8553 \text{ \AA}$ and $c = 14.1180 \text{ \AA}$. It can be observed that the spectrum of the surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders is almost the same as the spectra of the base one. The absence of any other signals in the spectra indicates the coated $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ is not crystal, but glass in nature. Both crystal lattice parameters a and c remained unchanged. Therefore, it was presumed that no boron was doped into the lattice of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

Fig. 2 shows the surface morphology of the base and surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. It seems very difficult to find some visible difference between two images, but the growth facets are exactly existing on the surface of the base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The surface morphology is very clean without any foreign phases. In comparison, the surface morphology of

Table 1
Surface composition of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders

Sample	Composition (at.%)				
	Li	Ni	Co	B	O
The base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	25.1	19.7	5.4	0.0	49.8
The surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	19.5	4.6	1.7	11.1	63.1

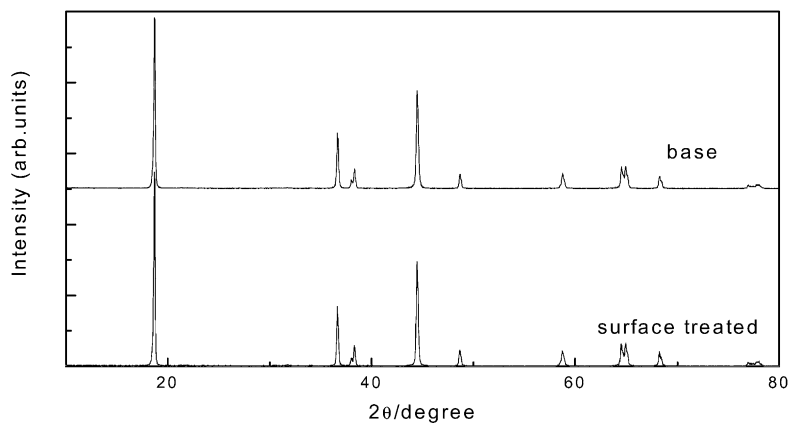


Fig. 1. X-ray diffraction pattern of the base and surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders.

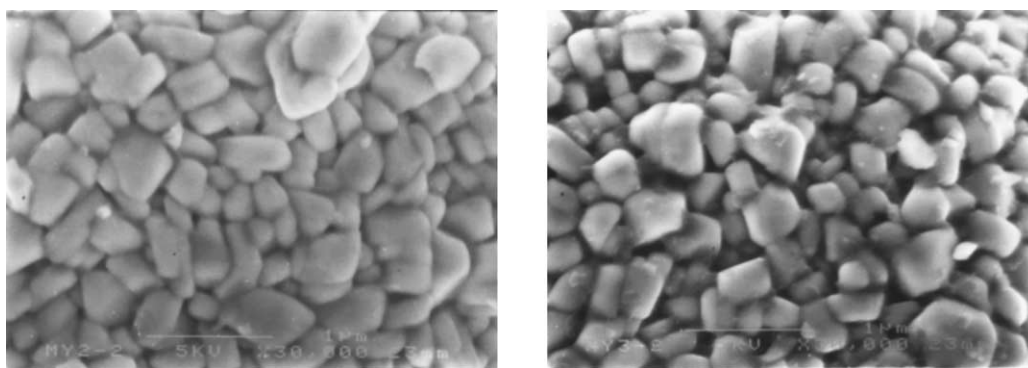


Fig. 2. SEM images of the base and surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

the surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is smooth and blurry, and most of the angular features have been round. The crystalline grains are obviously coated with a lot of infinitely small flakes. The above modification in morphology may be the result of presence of a surface glassy phase. The result corresponds to the result of XPS analysis, which shows $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ are enriched on the surface.

The specific surface area of the powders was determined by the BET method. The base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has an original surface area of $1.5 \text{ m}^2 \text{ g}^{-1}$. The addition of only 1.0 wt.% $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glassy phase results in the decrease of the surface area to approximately $1.0 \text{ m}^2 \text{ g}^{-1}$. This may result

from the glassy liquid phase sintering the particulate surfaces, thereby, removing high surface area and surface defects. Therefore, surface treatment cannot only reduce the interface of the cathode contacting directly with the electrolyte, but also decrease the specific surface area of the powders. Such a surface treatment should have a profound effect on the performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material.

It can be observed from Figs. 3 and 4 that the charge–discharge capacity and the cycle performance of the surface-treated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ both are much better than that of base one, especially at elevated temperature. At low temperature of 20°C , the base $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material has a first

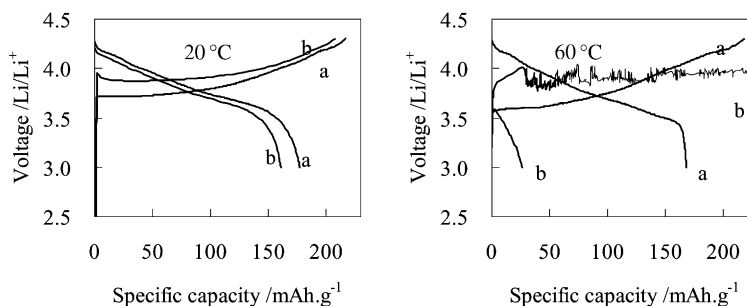


Fig. 3. Charge–discharge curves of the first cycle for (a) $\text{Li}/1.0 \text{ M LiPF}_6\text{-EC/DEC/surface-treated } \text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cell; and (b) $\text{Li}/1.0 \text{ M LiPF}_6\text{-EC/DEC/base } \text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cell. Cycling was carried out galvanostatically at constant charge–discharge current density of 0.5 mA cm^{-2} between 3.0 and 4.3 V at different temperature.

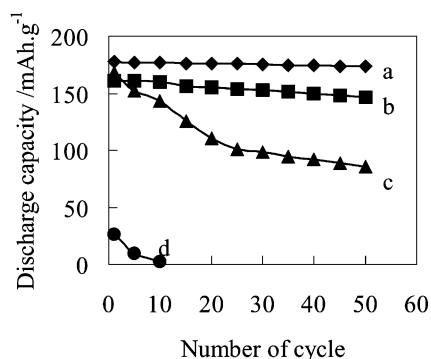


Fig. 4. Variation of specific discharge capacity with number of cycles for Li/1.0 M LiPF₆-EC/DEC/LiNi_{0.8}Co_{0.2}O₂ cells. Cycling was carried out galvanostatically at constant charge–discharge current density of 0.5 mA cm⁻² between 3.0 and 4.3 V: (a) using surface-treated LiNi_{0.8}Co_{0.2}O₂, tested at 20°C; (b) using base LiNi_{0.8}Co_{0.2}O₂, tested at 20°C; (c) using surface-treated LiNi_{0.8}Co_{0.2}O₂, tested at 60°C; and (d) using base LiNi_{0.8}Co_{0.2}O₂, tested at 60°C.

charge capacity of 208 mAh g⁻¹ followed by a discharge capacity of 161 mAh g⁻¹ with the irreversible capacity of 47 mAh g⁻¹ and reversible capacity loss of 9.3% in 50 cycles. In comparison, the surface-treated LiNi_{0.8}Co_{0.2}O₂ cathode material has a first charge capacity of 218 mAh g⁻¹ followed by a discharge capacity of 177 mAh g⁻¹ with the irreversible capacity of 39 mAh g⁻¹ and reversible capacity loss of 2.2% in 50 cycles. As observed in Fig. 3, at the same charge capacity, the surface-treated LiNi_{0.8}Co_{0.2}O₂ has lower charge voltage than the base one, while at the same discharge capacity, the former has higher discharge voltage than the latter. The higher charge–discharge capacity, lower irreversible capacity, better cycling stability, lower charge voltage and higher discharge voltage of the surface-treated LiNi_{0.8}Co_{0.2}O₂ cathode material are partly attributed to the Li₂O–2B₂O₃ coating. According to the reports [6,7], the Li₂O–2B₂O₃ coating is not a good electronic conductor, but a very good Li⁺ ionic conductor. The coating is so thin that it allows effective electron tunneling and does not isolate the surface-treated LiNi_{0.8}Co_{0.2}O₂ cathode material from charge transfer. It is expected that coating the LiNi_{0.8}Co_{0.2}O₂ particulate with the high Li⁺ ionic conductor may promote the Li⁺ transfer process through the interfaces between the particulate. As a result, the charge voltage is reduced, and the discharge voltage is increased as well.

On the other hand, the first cycle irreversibility is primarily related to the decomposition of electrolyte, which requires extra charge for oxidation. The higher discharge capacity and lower irreversible capacity of the surface-treated LiNi_{0.8}Co_{0.2}O₂ mainly should be the result of suppression of the electrolyte decomposition, which is due to the formation of a barrier film protecting the electrolyte oxidation from the catalytic effects of the delithiated LiNi_{0.8}Co_{0.2}O₂. The Li₂O–2B₂O₃ coating can also prevent the LiNi_{0.8}Co_{0.2}O₂ from corroding by the electrolyte, stabilize the structure of the charged LiNi_{0.8}Co_{0.2}O₂, and cut down the harmful by-products during the charge–discharge

cycling. Therefore, the surface-treated LiNi_{0.8}Co_{0.2}O₂ cathode material has better cycling stability than the base one.

In the strengthened charge–discharge experiment at elevated temperature of 60°C, the improvement is much more obvious as that indicated in Figs. 3 and 4. The base material only has a first discharge capacity of 26.1 mAh g⁻¹ if the charge process is cut-off when the charge capacity reaches the material's theoretical value of 274 mAh g⁻¹. The discharge capacity is quickly reduced to near 0 mAh g⁻¹ within 10 cycles. The poor characteristics at the elevated temperature are due to the more serious side reactions between the LiNi_{0.8}Co_{0.2}O₂ and electrolyte. In comparison, the surface-treated LiNi_{0.8}Co_{0.2}O₂ has stable electrode potential and charge current as well as monotonic charge–discharge curves during the cycling. The material still has a first charge capacity of 218 mAh g⁻¹ followed by a discharge capacity of 168 mAh g⁻¹. The material shows reversible capacity retention of more than 50% after 50 cycles.

In order to research the self-discharge phenomenon in a limited duration, another strengthened experiment has been done. The Li/1.0 M LiPF₆-EC/DEC/LiNi_{0.8}Co_{0.2}O₂ cells using the two kinds of cathode materials were fully charged and then stored at 20 and 60°C for 1 month, respectively. It was tested that the self-discharge rates of the cells using the surface-treated LiNi_{0.8}Co_{0.2}O₂ stored at 20 and 60°C are 6.0% per month and 18.0% per month, respectively. The self-discharge rates of the cell using the base LiNi_{0.8}Co_{0.2}O₂ stored at 20°C is more than 10.8% per month. The cell using the base LiNi_{0.8}Co_{0.2}O₂ stored at 60°C for 1 month lost almost all of its capacity. The results show that the surface treatment is effective in reducing the self-discharge. The lithium secondary batteries using the surface-treated LiNi_{0.8}Co_{0.2}O₂ cathode material can be stored more reliably and safely.

In addition, we found the separator and lithium metal in the tested cells using the base LiNi_{0.8}Co_{0.2}O₂ covering black substance, especially at elevated temperature. Though the composition of the black substance is not clear now, it may be the solute of the cathode material or the by-products created from the harmful interaction between the LiNi_{0.8}Co_{0.2}O₂ and liquid electrolyte. In comparison, the separator and lithium metal in the tested cells using the surface-treated LiNi_{0.8}Co_{0.2}O₂ remain clean. It can be concluded the Li₂O–2B₂O₃ coating does prevent the corrosion and dissolution of LiNi_{0.8}Co_{0.2}O₂.

4. Conclusions

The use of surface treatment is an effective way to improve the comprehensive performance of LiNi_{0.8}Co_{0.2}O₂ cathode material for lithium secondary batteries. The surface treatment is successful in minimizing the harmful side reactions within the batteries by placing a protective barrier layer between the oxidizing cathode material and the liquid electrolyte. The surface-treated LiNi_{0.8}Co_{0.2}O₂ cathode material has the advantage of higher charge–discharge capacity, lower

irreversible capacity, better cycling stability, less self-discharge rate, lower charge voltage, higher discharge voltage, especially the improved elevated temperature characteristics.

This surface treatment suggests a new approach to the development of cathodes for lithium secondary batteries. We believe that controlling the surface chemistry of electrode materials and the electrode/electrolyte interface is crucial to minimize side reactions within batteries. It is necessary to further research towards the design of better electrode/electrolytes interface.

Acknowledgements

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