



# Influence of surface modification on structure and electrochemical performance of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$

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## Abstract

The electrochemical stability of  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  is improved by sol–gel coating with an amorphous  $\text{SiO}_2$  film. This limits direct contact between  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  and electrolyte, and thus, effectively provides the structural stability for the electrochemically active intercalation compound  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ , resulting in improved specific capacity and cycling performance.

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*Keywords:* Secondary lithium batteries;  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ ; Surface modification

## 1. Introduction

Li ion batteries belong to a rapidly growing field as rechargeable power sources for room temperature consumer applications, since the commercialization of Sony's lithium-ion cell in 1990 [1–7]. However, harmful interactions between the active positive materials and the electrolyte in lithium secondary batteries deteriorate the performance of the cathode materials and the batteries [8–10]. In order to limit these harmful interactions, interest in surface-modified cathodes has increased due to their improved electrochemical behavior [8–11]. It is reported that thin film oxide coating ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ , etc.) on the powder surface has improved the electrochemical perfor-

mance of the electrochemically active intercalation compound ( $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$ , etc.) [9–13].  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ , a high-voltage cathode candidate, also suffers from harmful interaction at the surface [14,15]. In the present work, a  $\text{SiO}_2$  film has been coated onto the surface of the  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  cathode material by the sol–gel method using  $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ . The influence of surface modification on electrochemical performance of  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  is reported.

## 2. Experimental

$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  powders were prepared first by dissolving stoichiometric quantities of  $\text{Li}_2\text{CO}_3$ ,  $\text{Ni}_2(\text{OH})_2\text{CO}_3$ ,  $\text{Co}(\text{Ac})_2$  and  $\text{NH}_4\text{VO}_3$  in de-ionized water. Under vigorous stirring, saturated citric acid solution and polyethylene glycol solution were added and a brown xerogel was obtained after being heated

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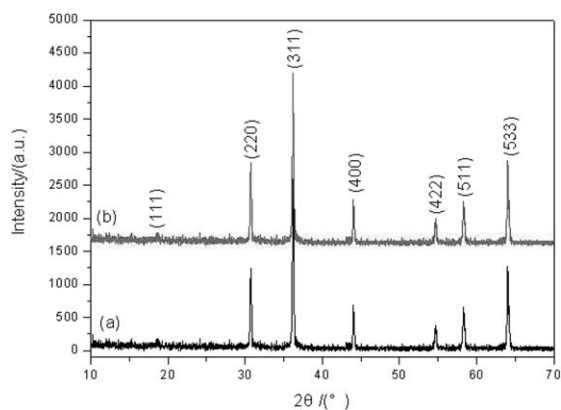


Fig. 1. XRD patterns of uncoated (a) and coated (b)  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ .

at 80–100 °C. The as-obtained xerogel was heated at 450 °C for 4 h and brown powders were attained.

The sol–gel coating of  $\text{SiO}_2$  on the powders was carried out as follows: 0.5 mol  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  powders were added to the mixed solution of 100 ml  $\text{Si}(\text{OCH}_2\text{CH}_3)_4$  and 0.01 mol ethanol under vigorous stirring and ultrasonic treatment at 40 °C, and then exposed in the air. After 3 days, the products obtained were heated at 600 °C for 10 h; this ultimately gave a yellowish powder.

X-ray diffraction (XRD) experiments were performed on a D/MAX-III X-ray diffractometer with  $\text{Cu K}\alpha$  radiation and a graphite monochromator. Transmission electron microscopy (TEM) images were attained using a JEM-100CX II scanning electron microscope at 80 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using an ESCALAB MK II multi-technique electron

spectrometer. The data were obtained at room temperature; typically, the operating pressure in the analysis chamber was below  $1 \times 10^{-8}$  Pa. The cathode preparation and the test cell were similar to as described in Ref. [14]. Li metal was used as the anode. The test cells containing 1 M  $\text{LiPF}_6\text{-EC-DEC}$  (1:1 volume ratio) were usually charged to 4.9 V and discharged to 2.8 V at a 0.15 C rate.

### 3. Results and discussion

The XRD patterns for uncoated and coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  are shown in Fig. 1. They are dominated by the (311) Bragg peak at  $2\theta = 36^\circ$ . Both of the XRD patterns display a weak (111) peak and a strong (220) peak, which indicate the predominant inverse spinel structure of  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  [14]. The presence of vanadium atoms on the tetrahedrally coordinated 8a site leads to the increase of the (220) intensity at the expense of the (111) peak [14,15]. The XRD pattern of coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  shows no any secondary phase, indicating that  $\text{SiO}_2$  exists in an amorphous state, or can react with  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  to give concentration gradients at the particle surface. The lattice constant  $a$  of the coated samples ( $a = 8.220 \pm 0.002 \text{ \AA}$ ) show no change compared to the uncoated one ( $a = 8.220 \pm 0.002 \text{ \AA}$ ), indicating that Si does not enter the  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  lattice.

The TEM images of uncoated and coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  are shown in Fig. 2. Spherical grains of uncoated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  are clear, with little impurity on their surface (Fig. 2a). In contrast, there is some deposit on the surface of spherical grains of

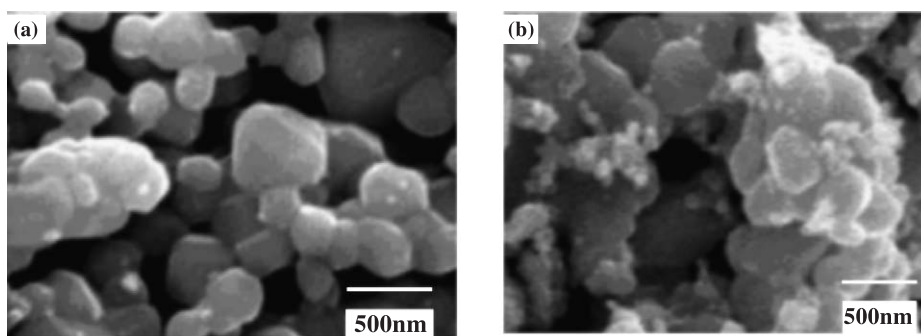


Fig. 2. TEM images of uncoated (a) and coated (b)  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ .

Table 1  
Surface composition of the coated and uncoated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$

Sample	Surface composition (atom%)					
	Li	Ni	Co	V	Si	O
uncoated $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$	12.41	6.19	6.22	12.39	0.00	62.79
coated $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$	7.21	3.49	3.51	7.19	21.52	57.08

coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  (Fig. 2b). Surface composition of uncoated and coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  were analyzed by XPS [16] and summarized in Table 1. Surface composition of uncoated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  is very near to the stoichiometric ratio of the elements in  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ , but the content of Li, Ni and Co on the surface of coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  decreases and a concentration of silicon (21.52 at.%) appears. There is only one chemical state for Si with a binding energy of 102.99 eV, corresponding to  $\text{SiO}_2$  [16]. A significant amount of Si atoms is thus distributed at the surface in the form of  $\text{SiO}_2$ , and Si atoms do not enter  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  in the form of a solid solution; this supports the result of the XRD, but is different from the solid solution forming on the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiCoO}_2$  material [11,13] or on the  $\text{ZrO}_2$ -coated  $\text{LiNiO}_2$  material [12].

The first charge-discharge curves and the capacity of the first ten cycles for uncoated and coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  are shown in Figs. 3 and 4, respectively. The first-charge capacity of uncoated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  is 90 mAh/g; it decreases to 38.7 mAh/g after ten cycles, where the cycling efficiency is 43%. However, the first-charge capacity of coated  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  is 100

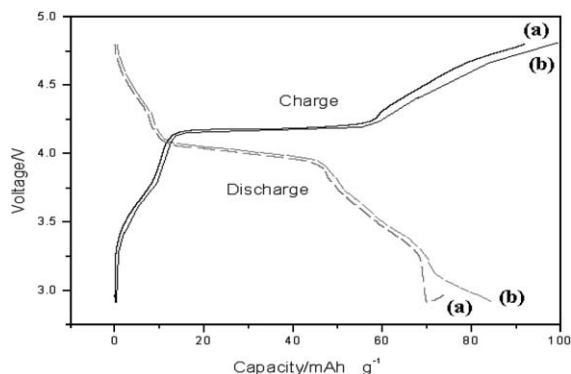


Fig. 3. First-charge/discharge curves of uncoated (a) and coated (b)  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ .

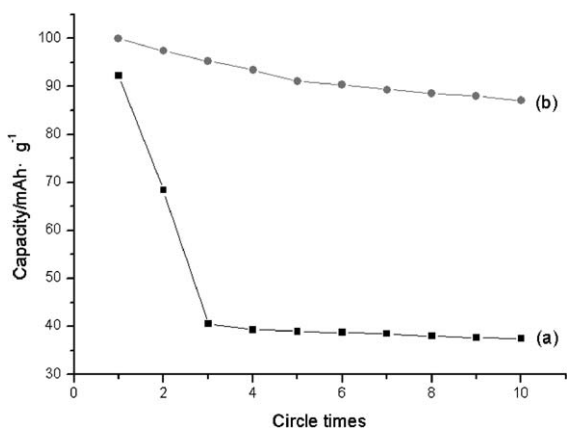


Fig. 4. Capacity of the first ten cycles of uncoated (a) and coated (b)  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ .

mAh/g, decreasing to 87 mAh/g after ten cycles; its cycling efficiency is 87%. It is shown that the specific capacity and cycling performance of  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  are improved significantly. The reason for this can be that contact area and side reactions between  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  and the electrolyte are effectively reduced through the surface modification by  $\text{SiO}_2$ . The structural stability of the electrochemically active intercalation compound  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  can thus effectively be engineered by the artificial formation of a thin  $\text{SiO}_2$  coating; the mechanism causing this improved performance needs to be further identified.

#### 4. Conclusions

An amorphous  $\text{SiO}_2$  film has been coated onto the surface of  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  cathode particles by the sol-gel method using  $\text{Si}(\text{CH}_2\text{CH}_3)_4$ . This surface modification improves specific capacity and cycling performance by the  $\text{SiO}_2$  layer reducing the contact area and side reactions between  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  and the electrolyte, thus providing structural stability of electrochemically active intercalation compound  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$ .

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