Journal of Alloys and Compounds 509 (2011) 3136–3140

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Electrochemical properties of the carbon-coated lithium vanadium oxide anode for lithium ion batteries

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ARTICLE INFO

Article history:
Received 13 August 2010
Received in revised form 2 December 2010
Accepted 3 December 2010
Available online 10 December 2010

Keywords:
Lithium vanadium oxide
Anode material
Carbon coating
Lithium-ion battery

ABSTRACT

Carbon-coated $Li_{1.1}V_{0.9}O_2$ powder was prepared by dissolving pure crystalline $Li_{1.1}V_{0.9}O_2$ powder in an ethanol solution containing 10 wt% sucrose and sintering it under an argon atmosphere. The structures of the bare and carbon-coated $Li_{1.1}V_{0.9}O_2$ powders were analyzed using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy. These powders were used as anode active materials for lithium ion batteries in order to determine the electrochemical properties via cyclic voltammetry (CV) and constant current methods. CV revealed the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode to have better reversibility during cycling than the bare $Li_{1.1}V_{0.9}O_2$ anode. Carbon-coated $Li_{1.1}V_{0.9}O_2$ also showed a higher specific discharge and charge capacities, as well as lower electrolyte and interfacial resistance properties. The observed specific discharge and charge capacities of the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode were 330 mAh/g and 250 mAh/g, respectively, in the first cycle. In addition, the cyclic efficiency of this cell was 75.8% in the first cycle. After 20 cycles, the specific capacity of the $Li_{1.1}V_{0.9}O_2$ anode was reduced to approximately 50% of its initial capacity, irrespective of the presence of a carbon coating.

1. Introduction

With the recent advances in electronic devices, high storage capacity and high power density materials have attracted considerable interest as alternatives to graphite as the anode material for lithium-ion batteries. In particular, lithium vanadate materials have been proposed as a new anode material to accommodate the lithium ion reversibly. It realizes a high specific capacity when discharged to 0.01 V vs. Li/Li^+ more than two times higher than that of commercial graphite [1,2]. However, the energy density of the cell based on some vanadate compounds could not be significantly enhanced because of its high working potential (more than 1.0 V vs. Li/Li^+) as compared to that of graphite (0.1 V vs. Li/Li^+) during the charge and discharge reactions [3,4]. Among these vanadate materials, $Li_{1.1}V_{0.9}O_2$ has a high specific capacity of 1200 mAh cm^{-3} on a volume basis and a low working potential of <0.3 V vs. Li/Li^+. Its potential as a high-density anode electrode has prompted intensive studies on its structure and valence state. $Li_{1.1}V_{0.9}O_2$ crystallizes in an ordered layered structure with Li^+ and V^{+3} ions occupying alternate (1 1 1) planes, and exhibits a hexagonal structure [5,6]. $Li_{1+x}VO_2$ has been synthesized using a spray pyrolysis technique [7]. This material showed a highly crystallized hexagonal structure. MnV_2O_6 materials have been synthesized via a hydrothermal method, which exhibits a very reversible capacity and excellent cycling performance at a high current density [8]. After lithium intercalation, $Li_{1.1}V_{0.9}O_2$ is converted to $Li_{2.1}V_{0.9}O_2$, corresponding to the *P*-3m1 space group, and the oxidation state of vanadium ions is reduced from V(III) to V(II). $Li_{1.1}V_{0.9}O_2$, because of its layered structure, shows a relatively low volume change of 25% as compared to that of highly capacitive Si- or Sn-based anode materials during the cycling process. However, the electrochemical properties of $Li_{1.1}V_{0.9}O_2$ may be insufficient for high-current applications without surface modifications. Carbon coatings can be an effective method to increase the electrical conductivity of $Li_{1.1}V_{0.9}O_2$ material.

In this study, a sucrose coating process was used to prepare a carbon-coated $Li_{1.1}V_{0.9}O_2$ anode via a simple solid-state reaction because carbon decreases the inter particle resistance of the active materials. The electrochemical properties of these anodes of lithium-ion batteries were examined using various analytical techniques.

2. Experimental

The active material, $Li_{1.1}V_{0.9}O_2$, was prepared through the conventional solid-state reaction described in our previous work [2]. A stoichiometric amount of Li_2CO_3 (Aldrich, 99.8%) and V_2O_3 (Alfa, 99.7%) was ball-milled in a planetary machine (Pulverisette 7, Fritsch) at a rotation speed of 250 rpm for 1 h. The ball-milled powders were sintered at 500 °C for 6 h in N_2 gas with 10 mol% H_2 gas and heated again to 1100 °C for 10 h at a heating rate of 5 °C/min under the same atmosphere to produce

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0925-8388/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2010.12.025

the $Li_{1.1}V_{0.9}O_2$ powder. The sample was then allowed to naturally cool down to room temperature. To synthesize carbon-coated $Li_{1.1}V_{0.9}O_2$, bare $Li_{1.1}V_{0.9}O_2$ powder was dissolved in an ethanol solution containing 10 wt% sucrose, and the resulting powder was dried at 80 °C for 24 h. The mixture was ground and sintered at 750 °C for 10 h under an argon atmosphere. The electrodes were prepared by mixing the active materials (90 wt%), conducting materials (Denka Black, 5 wt%), a poly(vinylidene fluoride) binder (5 wt%), and a 1-methyl-2-pyrrolidinone organic solvent in a high-speed mixer. The slurry was cast on a copper foil, dried at 80 °C in a vacuum oven for 24 h to remove the residual organic solvent, and then pressed using a rolling machine. The electrodes were assembled along with a lithium foil electrode using CR2032 coin cells in a dry room (dew point: −60 °C). A microporous polypropylene separator (Celgard 2400) was used. The electrolyte used was 1 M $LiPF_6$ in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (3:7 by volume). The crystal structure of the powder was analyzed using dispersive Raman spectroscopy (Nicolet Almega XR, Thermo Electron Corp.) and X-ray diffraction (XRD, Rigaku D/MAX-2500 V). The morphology of the powder was determined using scanning electron microscopy (SEM, Hitachi 4300) and transmission electron microscopy (TEM, FEI Tecnai F20). The ac impedance characteristics of the assembled cells were examined using an impedance gain phase analyzer (Solartron SI 1260) coupled with an electrochemical interface (Solartron SI 1286). The cells were tested by cyclic voltammetry and a galvanostatic mode at voltage range from 0.01 to 2.0 V vs. Li/Li^+ using a Maccor cycle system (S 4000, USA).

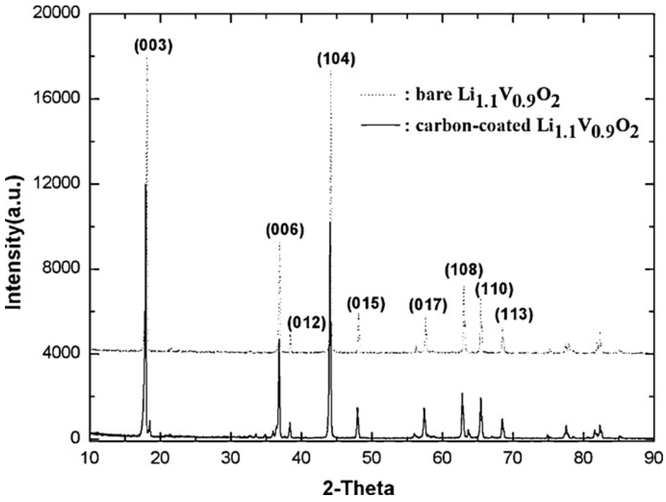
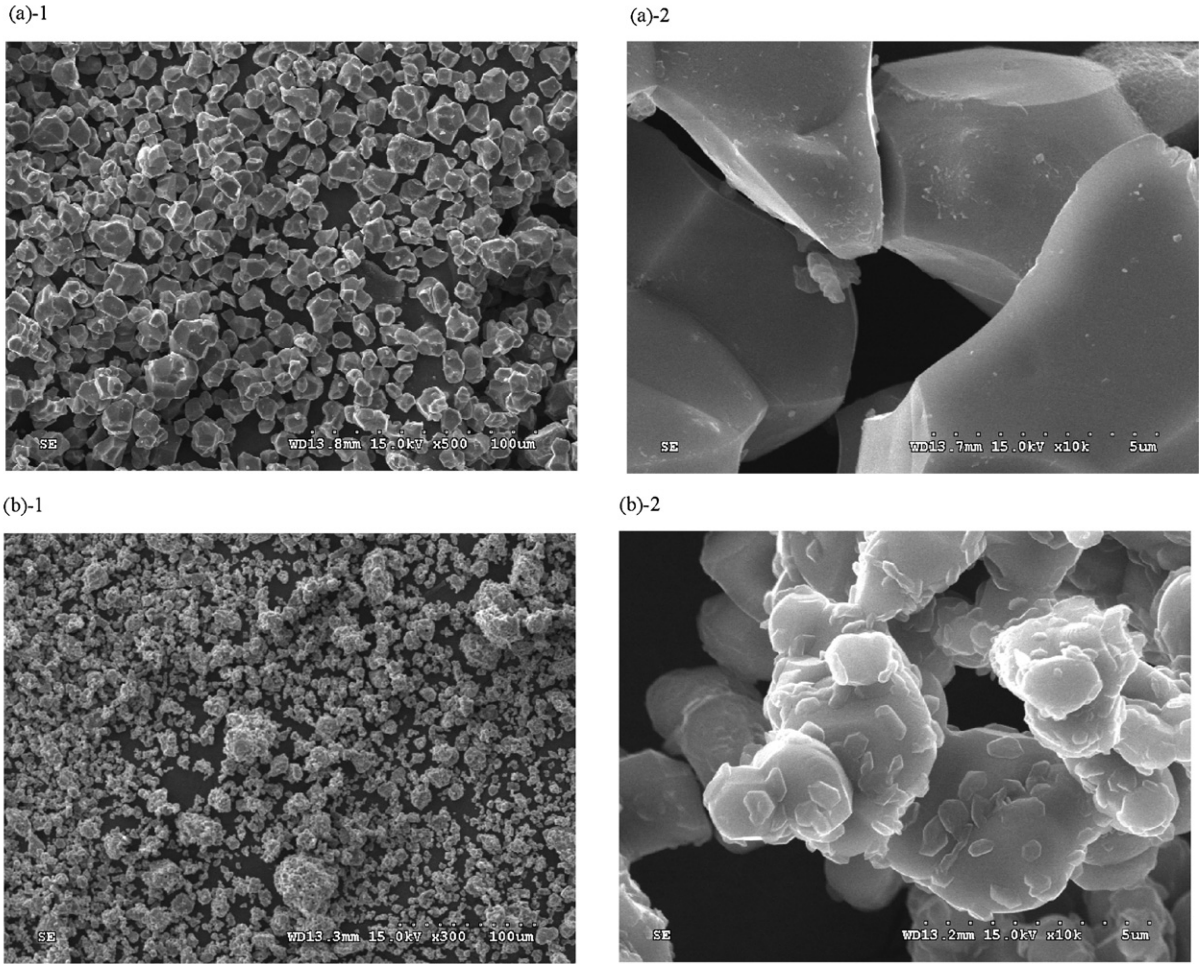


Fig. 1. XRD patterns of the bare $Li_{1.1}V_{0.9}O_2$ and carbon-coated $Li_{1.1}V_{0.9}O_2$ powders.

3. Results and discussion

Fig. 1 shows the XRD patterns of the bare and carbon-coated $Li_{1.1}V_{0.9}O_2$ powders. Both powders had the same hexagonal structure with the *R*-3m space group, irrespective of the presence of a carbon coating. The carbon content in the carbon-coated $Li_{1.1}V_{0.9}V_2$ powder was approximately 10 wt%. The SEM image of the carbon-coated $Li_{1.1}V_{0.9}O_2$ powder (Fig. 2) indicated a rough surface with a mean size of approximately 5–10 μm, while that of bare $Li_{1.1}V_{0.9}V_2$ indicated a flat surface with a mean size of approximately 10–20 μm. Carbon particles may deposit on the surface of $Li_{1.1}V_{0.9}O_2$ after the decomposition of sucrose, making the particle surface uneven. Fig. 3 shows the Raman spectrum of the carbon-coated $Li_{1.1}V_{0.9}O_2$ powder with a 514 nm excitation line. It shows sharp peaks centered at approximately 800 cm^{-1}, corresponding to a typical crystalline $Li_{1.1}V_{0.9}O_2$ phase, along with two broad


(a)-1

(a)-2

(b)-1

(b)-2

Fig. 2. SEM images of the bare $Li_{1.1}V_{0.9}O_2$ (a) and carbon-coated $Li_{1.1}V_{0.9}O_2$ (b) powders.

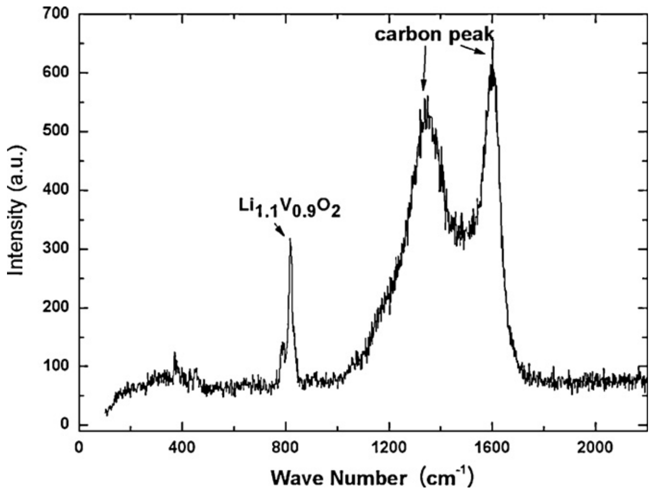


Fig. 3. Raman spectrum of the carbon-coated $Li_{1.1}V_{0.9}O_2$ powder.

peaks at 1350 cm^{-1} and 1590 cm^{-1}, indicating a carbon phase. It was reported that the V–O bonds are assigned to Raman stretching frequencies in the 600–800 cm^{-1} region [9]. The *D* (amorphous carbon) and *G* (graphitic carbon) bands for a pure carbon phase, which provides additional information on the structure and domain size of carbon materials, were observed at 1340 cm^{-1} and 1582 cm^{-1}, corresponding to the sp^3 (disordered carbon) and sp^2 (graphite carbon) stretching modes, respectively [10]. These two wide and broad peaks indicate that the carbon coating on the $Li_{1.1}V_{0.9}O_2$ particles is composed of crystalline graphite and amorphous carbon. The morphology of the surface was confirmed by TEM; the TEM images are shown in Fig. 4. The carbon-coated $Li_{1.1}V_{0.9}O_2$ particles display a thin layer on the particle surface, which is presumably a carbon layer. The thickness of the layer was not uniform but was estimated to be approximately 10 nm on average.

The cyclic voltammogram of the bare and carbon-coated $Li_{1.1}V_{0.9}O_2$ anodes, during the first cycles in the potential range of 0.01 V and 2 V vs. Li/Li^+, respectively, shows that the electrochemical reaction is highly irreversible at around 0.25 V vs. Li/Li^+

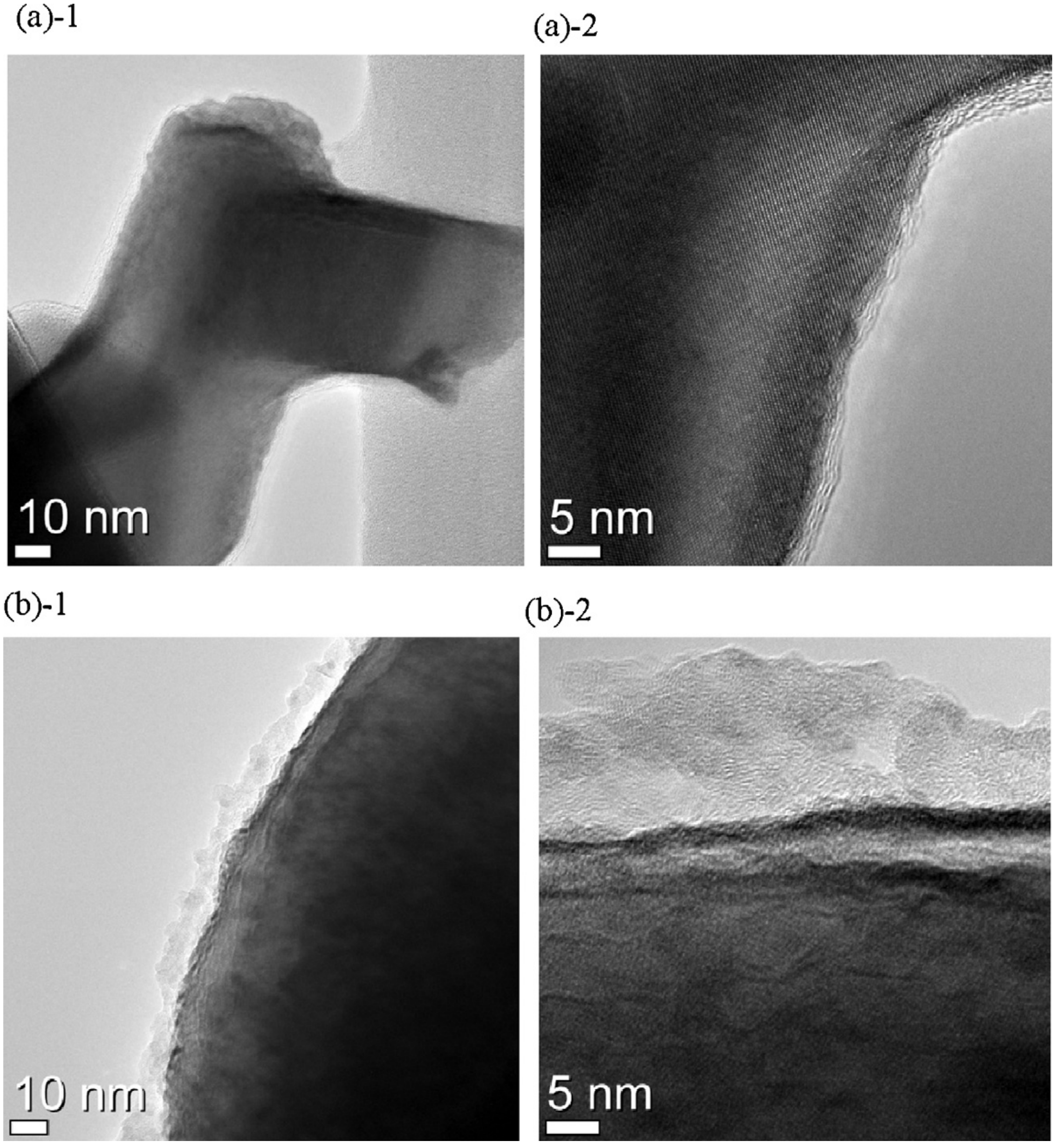


Fig. 4. TEM images of the bare $Li_{1.1}V_{0.9}O_2$ (a) and carbon-coated $Li_{1.1}V_{0.9}O_2$ (b) powders.

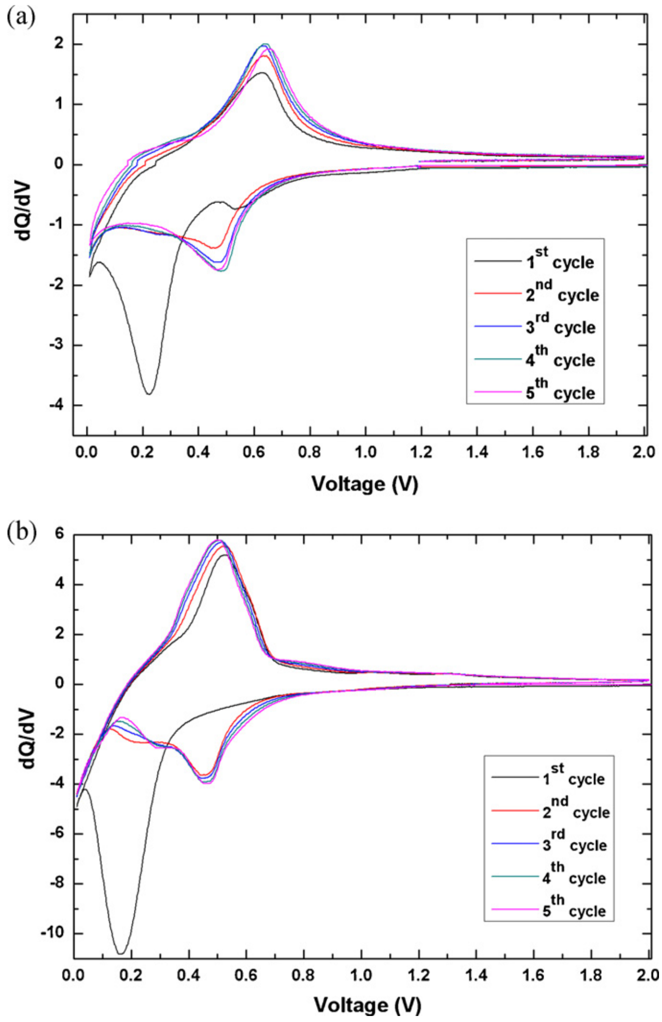


Fig. 5. Cyclic voltammograms of the bare $Li_{1.1}V_{0.9}O_2$ (a) and carbon-coated $Li_{1.1}V_{0.9}O_2$ (b) anodes.

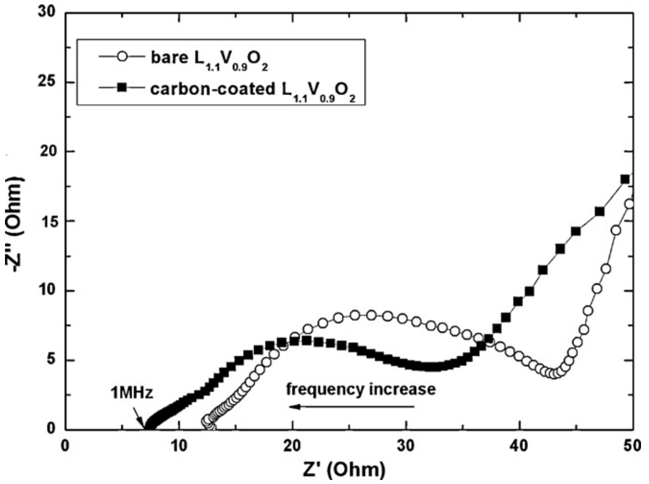


Fig. 6. Electrochemical impedance spectrum of the bare $Li_{1.1}V_{0.9}O_2$ and carbon-coated $Li_{1.1}V_{0.9}O_2$ anodes.

(Fig. 5). This irreversible capacity was attributed to the formation of a solid electrolyte interphase layer between the electrode and electrolyte. It was also considered that some species reacted with the $Li_{1.1}V_{0.9}O_2$ anode during the discharge. However, after the first cycle, this irreversible capacity disappeared and the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode showed a more reversible reaction than the bare $Li_{1.1}V_{0.9}O_2$ anode. To understand these phenomena, electrochemical impedance spectroscopy was performed over the frequency range of 0.3 Hz to 1 MHz after the initial cycle. The ac voltage used during the measurements was 10 mV. The impedance spectra of the bare and carbon-coated $Li_{1.1}V_{0.9}O_2$ anodes in Fig. 6 show the lines intercepting the real part at a high frequency, corresponding to the resistance of the electrolyte. In the case of the bare $Li_{1.1}V_{0.9}O_2$ anode, the resistance increased slightly due to the reactivity of the electrode and electrolyte. It is considered that the carbon layer plays a role preventing the reaction between the electrode and electrolyte. The carbon-coated $Li_{1.1}V_{0.9}O_2$ anode showed lower interfacial resistance than the bare $Li_{1.1}V_{0.9}O_2$ anode. The first semicircle at a high frequency represents the inter-particle contact resistance, such as that between the bare $Li_{1.1}V_{0.9}O_2$ anode/carbon and carbon/carbon contacts [11]. The second semicircle at the middle frequency increased due to the growth of a passive layer thickness for the bare $Li_{1.1}V_{0.9}O_2$ anode compared to the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode. The decrease in the diameter of the semicircles could decrease the contact resistance and passive layer thickness by carbon coating. The charge/discharge voltage curves of the bare $Li_{1.1}V_{0.9}O_2$ and carbon-coated $Li_{1.1}V_{0.9}O_2$ composite anode in Fig. 7 suggest that the specific charge/discharge capacity of the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode is higher than that of the bare $Li_{1.1}V_{0.9}O_2$ anode at a 0.1C rate (0.35 mA). In addition, the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode shows a distinct plateau potential at approximately 0.25 V during the charging, whereas the bare $Li_{1.1}V_{0.9}O_2$ anode showed a higher charge potential difference by 0.1 V, probably due to the increased polarization effect. The carbon layer might act as a stabilizer when lithium is inserted and extracted. Fig. 8 shows the cyclic performances of the bare and carbon-coated $Li_{1.1}V_{0.9}O_2$ anodes. The observed specific discharge and charge capacities of the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode were 330 mAh/g and 250 mAh/g in the first cycle. In the case of the bare $Li_{1.1}V_{0.9}O_2$ anode, the specific capacities were 275 mAh/g and 210 mAh/g for the same cycle. The initial coulombic efficiency of both the anodes was approximately 76%. The specific capacities of the $Li_{1.1}V_{0.9}O_2$ anodes were reduced to approximately 50% of the initial capacities after 20 cycles, irrespective of the presence of a carbon coating. There is no difference in the capacity retention after 20 cycles for either anode. The remaining lithium ions could not be extracted completely from the layered $Li_{2.1}V_{0.9}O_2$ anode by an electrochemical method. The fading of the capacity may be

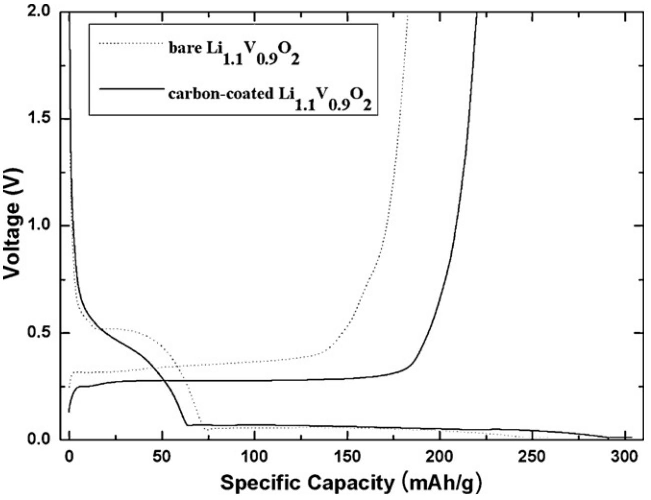


Fig. 7. Initial charge/discharge voltage curves of the bare $Li_{1.1}V_{0.9}O_2$ and carbon-coated $Li_{1.1}V_{0.9}O_2$ anodes.

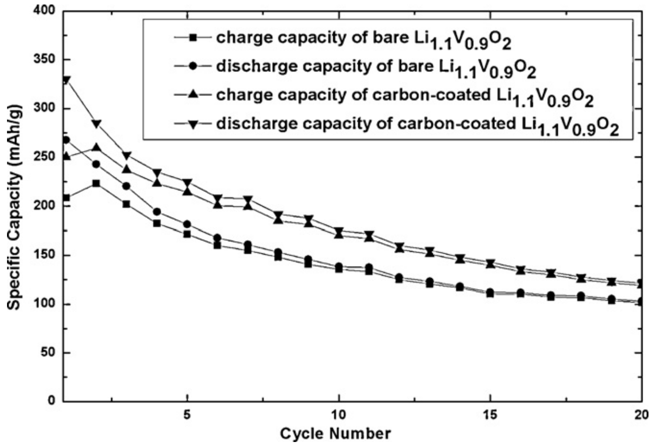


Fig. 8. Cyclic performances of the bare $Li_{1.1}V_{0.9}O_2$ and carbon-coated $Li_{1.1}V_{0.9}O_2$ anodes.

mainly attributed to the difficulty in lithium extraction. It has been reported that there is no structural transformation between before and after cycling [2].

4. Conclusions

$Li_{1.1}V_{0.9}O_2$ was synthesized by planetary ball-milling and a solid-state reaction, and was successfully carbon-coated via the decomposition process of sucrose at high temperatures. The presence of carbon in the carbon-coated $Li_{1.1}V_{0.9}O_2$ powder was confirmed using Raman spectroscopy and TEM, which indicated the existence of a carbon layer; on the other hand, there was no distinctive difference in the XRD pattern between the bare $Li_{1.1}V_{0.9}O_2$ and carbon-coated $Li_{1.1}V_{0.9}O_2$ powders. Cyclic voltammetry of the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode revealed enhanced reversibility compared to the bare $Li_{1.1}V_{0.9}O_2$ anode. The carbon-coated $Li_{1.1}V_{0.9}O_2$ anode also showed a higher specific discharge and charge capacities, as well as lower electrolyte resistance and interfacial resistance properties, making it a suitable alternative candidate as an anode material in lithium batteries. Further studies to determine the cause of the decrease in the specific capacity of the carbon-coated $Li_{1.1}V_{0.9}O_2$ anode after several cycles and to improve the stability are currently underway.

Acknowledgements

This study was supported by “The Middle and Long-term Technology Development Project” of the Ministry of Knowledge Economy of Korea and by the World Class University program through the National Research Foundation of Korea funded by the MEST (R33-2008-000-10025-0).

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