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Improvement of $LiCoO_2$ cathodes by using $Ag_2V_4O_{11}$ as an additive

X. CAO*, J. LIU, J. WAN, L. XIE, X. YAN, H. WANG

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou, 450001 P.R. China

$LiCoO_2/Ag_2V_4O_{11}$ composites were fabricated as cathode materials for lithium ion batteries by mechanical mixing of commercial $LiCoO_2$ and $Ag_2V_4O_{11}$ powders. The underlying principle of this idea was that the metallic silver particles were formed and acted as a conducting matrix when $Ag_2V_4O_{11}$ cathode was electrochemically reduced which could significantly increase the electronic conductivity and decrease the polarization of cathode materials. The structure, morphology and electrochemical performance of bare $LiCoO_2$ and $LiCoO_2/Ag_2V_4O_{11}$ composites were analyzed by XRD, SEM and charge-discharge test of CR2016 coin cells. The results show that a low amount of $Ag_2V_4O_{11}$ additive can effectively enhance the discharge capacity and cycleability of $LiCoO_2$. The composite containing 3 wt. % of $Ag_2V_4O_{11}$ exhibits a higher discharge capacity and better cycle life than bare $LiCoO_2$.

Key words: *lithium-ion batteries; electrochemical performance; $LiCoO_2$; $Ag_2V_4O_{11}$ additive*

1. Introduction

Layered $LiCoO_2$ oxide has been widely applied as cathode active material for Li -ion batteries. Ease of preparation, excellent electrochemical properties and high tap density make it the most commercially used cathode material. In the upcoming years, $LiCoO_2$ will continue to maintain its leading position in terms of market share, despite increasing research into alternative materials such as $LiNi_xCo_{1-x}O_2$, $LiNi_xMn_yCo_{1-x-y}O_2$ and $LiFePO_4$ [1]. However, in general, the maximum delivery capacity of $LiCoO_2$ is around half of its theoretical value (274 mAh/g) due to a large structural change that occurs during the Li^+ deintercalation process [2]. Therefore, how to increase the practical usable capacity of $LiCoO_2$ is a very important and exciting problem.

Nevertheless, the electronic conductivity of $LiCoO_2$ powder is low, and thus $LiCoO_2$ must be well-combined with electro-conductive additives, such as carbon black and acetylene black, for use as active cathode materials. Usually, the total

*Corresponding author, e-mail: caoxy@haut.edu.cn

amount of carbon black and binder must be more than 15% of the total weight of the electrode materials in order to maintain a good conductivity and a mechanical stability of the cathodes [3]. On the other hand, use of excess electro-conductive additives will incur a fall in the energy and power densities for lithium ion batteries. In order to reduce the inert weight of carbon black and improve the electrochemical performance of the cathodes, use of electronically conducting matrices such as polymers, metallic particles and metal fibres has been proposed [3–6].

More recently, Wen et al. [4] developed a novel method with $AgNO_3$ as a starting material to prepare an $LiCoO_2$/Ag composite cathode material for improving the discharge properties such as discharge capacity and rate-capability. It is found that the electronic conductivity of the $LiCoO_2$/Ag composite is significantly enhanced compared with bare $LiCoO_2$, which contributes to a reduced charge-transfer resistance. However, this method greatly suffers from its implementational complexity, because it requires an extra thermal decomposition of the mixture of $LiCoO_2$ and $AgNO_3$ in order to obtain the $LiCoO_2$/Ag composite. It is well known that $Ag_2V_4O_{11}$ is a very important cathode material for lithium primary batteries, and that the Li–$Ag_2V_4O_{11}$ battery system has been used as a power source for implantable cardiac defibrillators (ICDs) [7]. With regard to the discharge characteristics of $Ag_2V_4O_{11}$ cathodes, it is widely acknowledged that metallic silver particles are formed during early states of discharge [7]. However, metallic silver cannot be completely oxidized to Ag^+ and returned to $[V_4O_{11}]$ layers when an $Ag_2V_4O_{11}$ cathode is recharged in terms of ex-situ XRD of cycled $Ag_2V_4O_{11}$ electrode [8]. Considering this fact, we developed a simple technique by mixing the commercial $LiCoO_2$ and $Ag_2V_4O_{11}$ powders and performing a particular charge-discharge regime for improving the charge-discharge properties of $LiCoO_2$. The structure, morphology and electrochemical properties of bare $LiCoO_2$ and $LiCoO_2$/$Ag_2V_4O_{11}$ composites are analyzed by XRD, SEM and a charge-discharge test of CR2016 coin cells.

2. Experimental

Commercial $LiCoO_2$ powder from Hunan Reshine New Material Co., Ltd, China, was used as a bare material for the preparation of $LiCoO_2$/$Ag_2V_4O_{11}$ composites. $Ag_2V_4O_{11}$ and commercial $LiCoO_2$ powders at various weight ratios (3, 5 and 9 wt. % of $Ag_2V_4O_{11}$) were homogeneously mixed by mechanical pestling in an agate mortar. The samples were designated as $LiCoO_2$/$Ag_2V_4O_{11}$-3, $LiCoO_2$/$Ag_2V_4O_{11}$-5 and $LiCoO_2$/$Ag_2V_4O_{11}$-9, respectively.

$Ag_2V_4O_{11}$ powders were prepared by the rheological phase method, as described previously [9]. Stoichiometric ratios of Ag_2CO_3 and NH_4VO_3 were mixed thoroughly by grinding in an agate mortar. The solid-liquid rheological body (muddy state) was obtained by adding distilled water dropwise. Then the rheological body was transferred to a cylindrical, Teflon-lined, stainless autoclave. The sealed autoclave was heated in table-drying and air circulation oven at 90 °C for 5 h and then dried at 120 °C for 8 h. The resulting yellow precursor was obtained by grinding the air-dried

rheological body. Finally, using an alumina crucible as container, the precursor was heated in a muffle furnace (Nabertherm, N7/H) at 500 °C in air for 10 h to obtain the final $Ag_2V_4O_{11}$ powders.

X-ray diffraction (XRD) analysis of the materials was carried out on an XRD-Pert Pro diffractometer (XPERT PRO MPD, Netherlands) with CoK_α radiation (λ = 1.78901 Å). The morphological feature of the so-prepared powders was observed on the SEM- JSM6380LA (JEOL, Japan). The working electrodes were composed of the $LiCoO_2/Ag_2V_4O_{11}$ composite powders, acetylene black and polytetrafluoethylene (PTFE) binder at the weight ratio of 80:10:10. The stainless-steel meshes were used as the current collectors. The CR2016 coin cells were assembled with pure lithium foil as counter electrodes, Celgard-2400 as the separator, 1 mol/dm^3 $LiClO_4$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (v/v, 1:1) as the electrolyte. All the coin cells were assembled in a dry glove box and tested on a multichannel Neware-battery tester (Neware, Shenzhen) at the ambient temperature. The operational capacity of $Ag_2V_4O_{11}$ is mainly under 3 V but there is hardly any capacity below 3 V for $LiCoO_2$. Therefore, the $LiCoO_2/Ag_2V_4O_{11}$ composite cathode was initially discharged down to a cut-off voltage of 2 V in order to obtain a large number of metallic silver particles. Subsequently, a normal charge-discharge test was cycled at the constant current rate of 30 mA/g (ca. 1.0 mA/cm^2) in the range of 3–4.3 V.

3. Results and discussion

The XRD patterns of the commercial $LiCoO_2$ powder and the $LiCoO_2/Ag_2V_4O_{11}$ composites are presented in Fig. 1. All the characteristic diffraction peaks of $LiCoO_2$ have been marked with asterisks in Fig. 1, curve d, and correspond to a well-defined hexagonal layered structure. Additionally, the characteristic diffraction peaks of $Ag_2V_4O_{11}$ powder are also found, though they are almost submerged by the baselines of XRD patterns due to a relatively higher amplitude of the $LiCoO_2$ diffraction peaks. The inset of Fig. 1d illustrates an expanded view of local XRD patterns of $Ag_2V_4O_{11}$ in the range of 22–40° in 2θ. Obviously, $Ag_2V_4O_{11}$ cannot be doped in the layered structure of $LiCoO_2$, and the $Ag_2V_4O_{11}$ containing specimen was just a composite of the $Ag_2V_4O_{11}$ and $LiCoO_2$ powders.

SEM micrographs of bare $LiCoO_2$ and $LiCoO_2/Ag_2V_4O_{11}$ composites are shown in Fig. 2. Bare $LiCoO_2$ in Fig. 2a clearly demonstrates the original particle shape of $LiCoO_2$, and its surface is smooth. Three composite samples in Figs. 2b–d reveal that the particle shape of $LiCoO_2$ is not changed. Moreover, it is clearly observed that $Ag_2V_4O_{11}$ powders, as submicrometric particles, are highly dispersed on the surface of the $LiCoO_2$ powders. The higher the $Ag_2V_4O_{11}$ content in the powder, the greater is the surface coverage of $LiCoO_2$ by the $Ag_2V_4O_{11}$ particles. The XRD and SEM results confirm the assumption that the addition of $Ag_2V_4O_{11}$ powder does not modify the ordered layer structure of $LiCoO_2$.

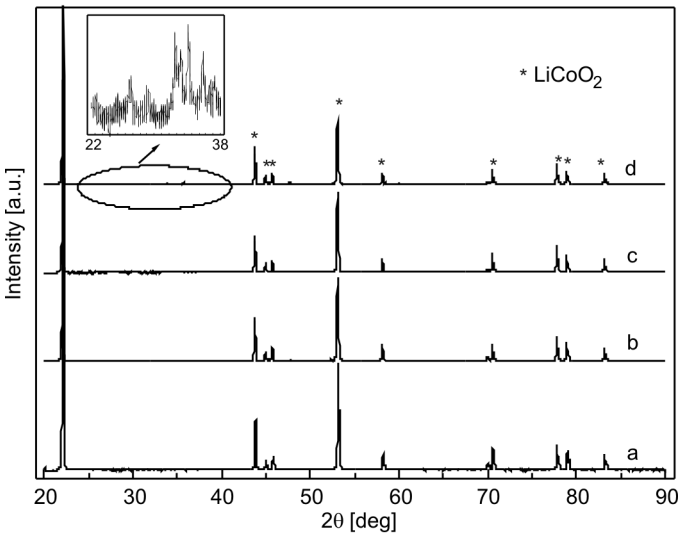

Fig. 1. XRD patterns of bare $LiCoO_2$ (a) and of $LiCoO_2/Ag_2V_4O_{11}$ composites of various $Ag_2V_4O_{11}$ contents: 3 wt. % (b), 5 wt. % (c), 9 wt. % (d)

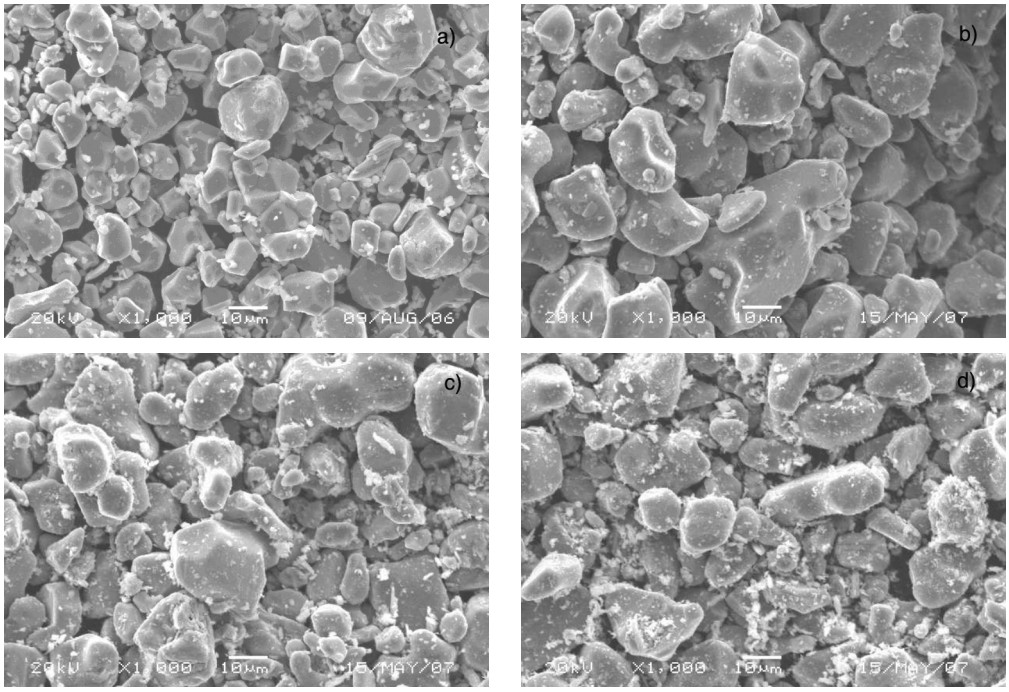

Fig. 2. SEM micrographs of bare $LiCoO_2$ (a) and of $LiCoO_2/Ag_2V_4O_{11}$ composites of $Ag_2V_4O_{11}$ contents: 3 wt. % (b), 5 wt. % (c), 9 wt. % (d)

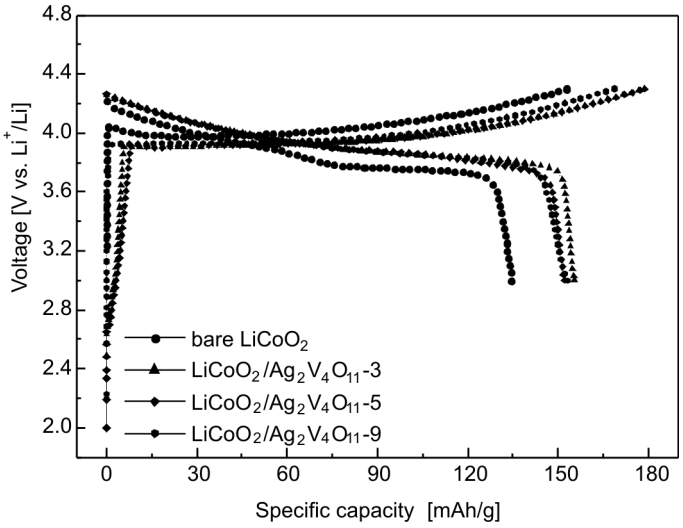

Fig. 3. Initial charge-discharge curves of bare $LiCoO_2$ and of $LiCoO_2/Ag_2V_4O_{11}$ composites of various $Ag_2V_4O_{11}$ contents

Figure 3 shows the initial charge-discharge curves of bare $LiCoO_2$ and of the $LiCoO_2/Ag_2V_4O_{11}$ composites. From the curves, we can see that bare $LiCoO_2$ has an initial discharge capacity of 134.5 mAh/g. However, for the $LiCoO_2/Ag_2V_4O_{11}$-3, $LiCoO_2/Ag_2V_4O_{11}$-5 and $LiCoO_2/Ag_2V_4O_{11}$-9 composites, the initial discharge capacities are equal to 155.4, 152.1 and 153.3 mAh/g, respectively. The initial discharge capacities of the $LiCoO_2/Ag_2V_4O_{11}$ composites are increased in all cases compared with that of bare $LiCoO_2$. In addition, the discharge plateaus of the $LiCoO_2/Ag_2V_4O_{11}$ composites are much higher than that of bare $LiCoO_2$ but, on the other hand, the charge plateaus of the $LiCoO_2/Ag_2V_4O_{11}$ composites are much lower than that of bare $LiCoO_2$. This observation indicates that the $LiCoO_2/Ag_2V_4O_{11}$ composites undergo a depressed electrode polarization during the charge-discharge process. The likely reason for the improved capacity should correspond strongly to the special discharge-charge regime. When the discharge procedure was first performed for $LiCoO_2/Ag_2V_4O_{11}$ composites with a cut-off voltage of 2 V, the metallic silver particles were formed. Such particles uniformly coated on $LiCoO_2$ may act as an electronic conductor, enhancing the surface intercalation reaction and decreasing the polarization of electrodes.

The selective charge-discharge curves of bare $LiCoO_2$ and $LiCoO_2/Ag_2V_4O_{11}$-3 composite are presented in Fig. 4. Charge–discharge curves of bare $LiCoO_2$ display only one plateau, corresponding to the intercalation/deintercalation of Li^+ into/out of the layered $LiCoO_2$. The shape of charge–discharge curves for various cycles is similar, and the discharge capacity of the 10th cycle is 135.3 mAh/g. However, the $LiCoO_2/Ag_2V_4O_{11}$-3 composite exhibits a better charge–discharge performance in comparison with bare $LiCoO_2$. The charge curves of the $LiCoO_2/Ag_2V_4O_{11}$-3 composite for different cycles almost overlap each other and the discharge capacities of the 7th

and 10th cycles are 153.4 and 153.7 mAh/g, respectively, which indicates that the Li-CoO_2/$Ag_2V_4O_{11}$-3 composite has excellent electrochemical stability. It is noteworthy that the discharge curves of the $LiCoO_2$/$Ag_2V_4O_{11}$-3 composite display two plateaus despite its imperceptibility which will be proved later in the differential capacity curve.

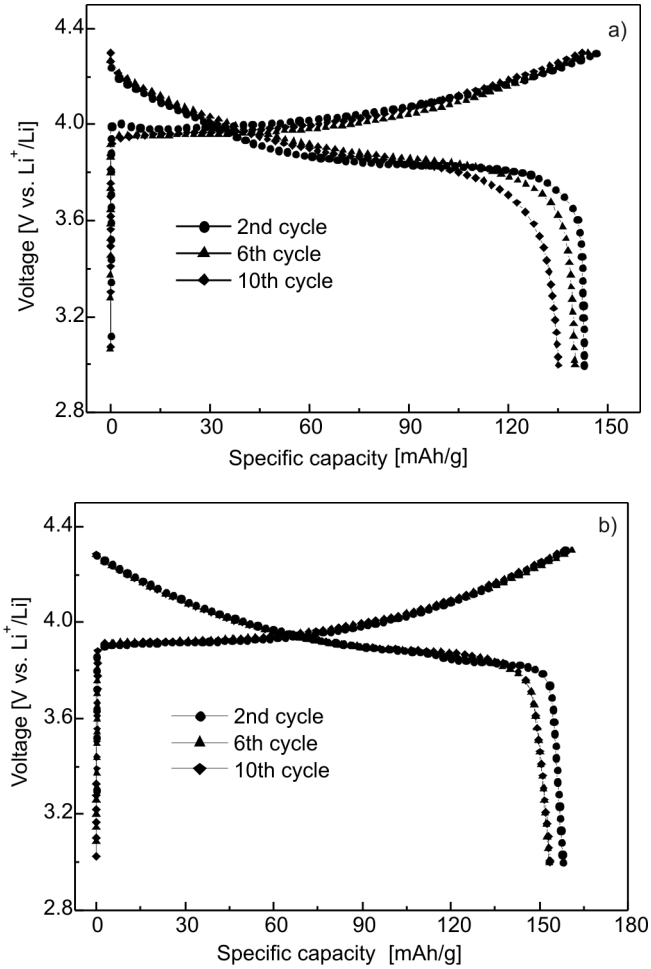

Fig. 4. Selective charge–discharge curves of a) bare $LiCoO_2$, and b) $LiCoO_2$/$Ag_2V_4O_{11}$-3 composite

The differential capacity curves of bare $LiCoO_2$ and the $LiCoO_2$/$Ag_2V_4O_{11}$-3 composite calculated from the 2nd charge-discharge curve are shown in Fig. 5, which emphasizes the details of the voltage curves. As shown in Fig. 5, there is one pair of peaks in the differential capacity curves for bare $LiCoO_2$, which is characteristic of the layered $LiCoO_2$ system and corresponds to the plateaus in the charge/discharge curves. It is interesting to observe a well defined reduction peak at about 3.89 V for the Li-

$CoO_2/Ag_2V_4O_{11}$-3 composite. It may be ascribed to the reduction of Ag^+ to Ag, because the redox reaction of the Ag^+/Ag couple still takes place between 3.0 and 4.3 V. This reduction peak is considered to be favourable because the electronic conductivity of $LiCoO_2/Ag_2V_4O_{11}$-3 composite is increased during the discharge. However, the oxidation peak attributed to the Ag^+/Ag couple is not observed in Fig. 5. A detailed investigation into the functional mechanism of $Ag_2V_4O_{11}$ in $LiCoO_2/Ag_2V_4O_{11}$ composites is currently in progress.

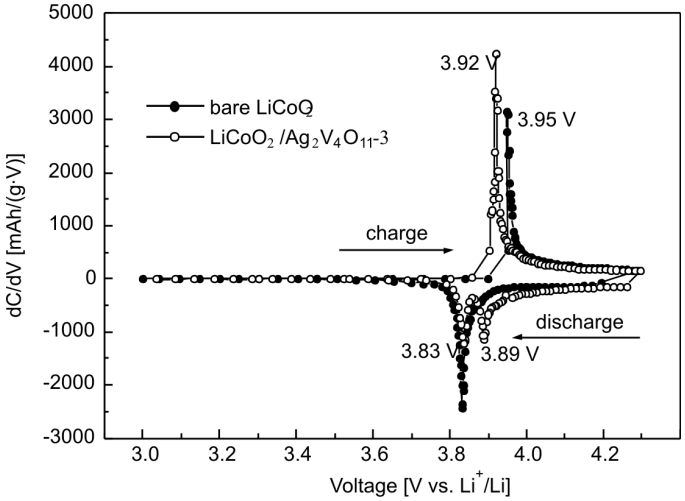

Fig. 5. Differential capacity vs. voltage curves for bare $LiCoO_2$ and $LiCoO_2/Ag_2V_4O_{11}$-3 composite

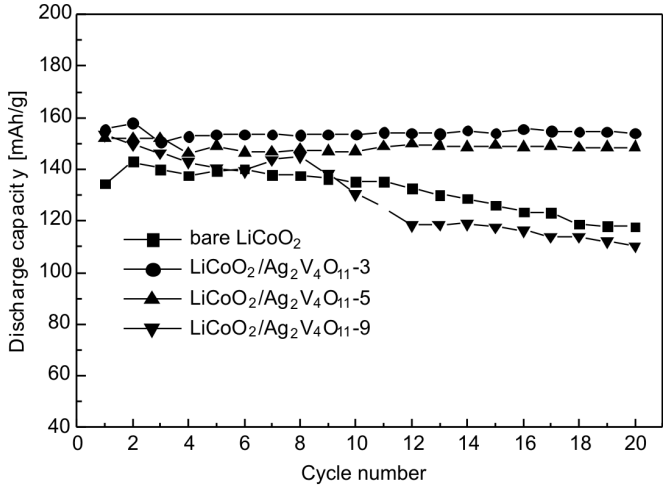

Fig. 6. Galvanostatic cycling of bare $LiCoO_2$ and $LiCoO_2/Ag_2V_4O_{11}$ composites at 30 mA/g between 3.0 and 4.3 V

The dependence of discharge capacity on the number of cycles for the materials collected at the current rate of 30 mA/g between 3.0 and 4.3 V is shown in Fig. 6. The stability of the $LiCoO_2/Ag_2V_4O_{11}$-3 and $LiCoO_2/Ag_2V_4O_{11}$-5 composites is excellent compared to bare $LiCoO_2$, though the profile of the discharge capacity follows a decreasing trend in function of increasing $Ag_2V_4O_{11}$ powder content. The $LiCoO_2$ /$Ag_2V_4O_{11}$-3 composite exhibits a stable discharge capacity of about 153.5 mAh/g within 20 cycles. In comparison, the discharge capacity of the $LiCoO_2/Ag_2V_4O_{11}$-5 composite is decreased but still stabilizes at about 148 mAh/g after 20 cycles. However, cycling the $LiCoO_2/Ag_2V_4O_{11}$-9 composite cell leads to rapid capacity fading after 10 cycles. This phenomenon should be attributed to the charge-discharge characteristics of the $Ag_2V_4O_{11}$ cathode. When the content of $Ag_2V_4O_{11}$ powder is low, the metallic silver particles formed during the discharge serve as a conducting matrix and increase the conductivity of the $LiCoO_2$ material. On the other hand, the structural character of $Ag_2V_4O_{11}$ is a very important factor that affects the electrochemical performance of $LiCoO_2/Ag_2V_4O_{11}$ composite and cannot be neglected when the content of $Ag_2V_4O_{11}$ powder is high. Long-term cycling in the silver reduction-oxidation region incurs a large volume change of cathode material, which probably results in rapid capacity fading [7]. Thus, an appropriate amount of $Ag_2V_4O_{11}$ additive is essential to improve the electrochemical performance of $LiCoO_2$.

4. Conclusions

A novel method is described for the preparation of $LiCoO_2/Ag_2V_4O_{11}$ composites by a simple mechanical mixing procedure. The low content of $Ag_2V_4O_{11}$ additive has been proved to be favourable to the discharge capacity and the cycleability of $LiCoO_2$. The composite containing 3 wt. % of $Ag_2V_4O_{11}$ exhibits the first discharge capacity as high as 155.4 mAh/g in the range of 3.0–4.3 V at the current rate of 30 mA/g and remains at a stable discharge capacity of about 153.5 mAh/g within 20 cycles, which is much higher than that of bare $LiCoO_2$. Therefore, we believe that this method not only provides an alternative to improving the electrochemical performance of $LiCoO_2$, but also is feasible in preparing other improved $LiCoO_2$ composites by adopting other silver vanadium oxides such as $AgVO_3$ and $Ag_{1.2}V_3O_8$.

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References

[1] TARASCON J.M., ARMAND M., Nature, 414 (2001), 359.
[2] ALCANTARC R., LAVELA P., TIRADO J.L., J. Solid State Chem., 134 (1997), 265.
[3] FENG C.Q., CHEW S.Y., GUO Z.P., WANG J.Z., LIU H.K., J. Power Sources, 174 (2007), 1095.

[4] HUANG S.H., WEN Z.Y., YANG X.L., GU Z.H., XU X.H., J. Power Sources, 148 (2005), 72.
[5] CROCE F., EPIFANIO A., HASSOUN J., DEPTULA A., OLCZAC T., SCROSATI B., Electrochem. Solid State Lett., 5 (2002), A47.
[6] AHN S., KIM Y., KIM K. J., KIM T. H., LEE H., KIM M. H., J. Power Sources, 81–82 (1999), 896.
[7] WEST K., CRESPI A.M., J. Power Sources, 54 (1995), 334.
[8] CAO X.Y., Ph.D. Thesis, Wuhan University, China, 2006.
[9] CAO X.Y., ZHAN H., XIE J.G., ZHOU Y.H., Mater. Lett., 60 (2006), 435.

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