Rapid Communication

Significant effect of electron transfer between current collector and active material on high rate performance of $Li_4Ti_5O_{12}$*

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The rate and cycling performances of the electrode materials are affected by many factors in a practical complicated electrode process. Learning about the limiting step in a practical electrochemical reaction is very important to effectively improve the electrochemical performances of the electrode materials. $Li_4Ti_5O_{12}$, as a zero-strain material, has been considered as a promising anode material for long life Li-ion batteries. In this study, our results show that the $Li_4Ti_5O_{12}$ pasted on Cu or graphite felt current collector exhibits unexpectedly higher rate performance than on Al current collector. For $Li_4Ti_5O_{12}$, the electron transfer between current collector and active material is the critical factor that affects its rate and cycling performances.

Keywords: $Li_4Ti_5O_{12}$, current collector, electron transfer, Li-ion batteries

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1. Introduction

Rechargeable Li-ion batteries have become the vital power sources for varieties of portable electronic devices and the promising candidate power for electric vehicles (EVs) and large scale energy storage, due to their highest energy density among secondary batteries.[1−4] However, the performances of current Li-ion batteries cannot meet the requirements for high power density, long cycling life and high safety in the applications of EVs and energy storage. Besides hunting for novel electrode materials to meet the above requirements, it is also important to ascertain the kinetic mechanism during the electrochemical reactions in Li-ion batteries. Taberna *et al.*[5] reported that the rate performance of Fe_3O_4 plating on Cu nano-architectured rod array was greatly improved, since Cu nano-architectured current collector effectively enhanced the kinetics during the electrochemical reactions of Fe_3O_4. In addition, Wu *et al.*[6] reported that carbon-coated aluminum can enhance the power properties of $LiFePO_4$. Therefore, the current collector is of great importance to affect the kinetics between active material and current collector. In recent years, $Li_4Ti_5O_{12}$ as a zero-strain insertion material has attracted great attention in power batteries for EVs and energy storage for green grid.[7,8] Extensive efforts have been made to improve its rate performance, for its poor electronic conductivity, via reducing its particle size and coating conductive materials on its surface.[9−12] However, little work has been done to explore the electron transfer between $Li_4Ti_5O_{12}$ and current collector. In this paper, we present our recent work on the significant effect of favourable electron transfer between active material and current collector on the kinetic performance of $Li_4Ti_5O_{12}$ and its mechanism.[13]

2. Experiment

The porous $Li_4Ti_5O_{12}$ sample prepared by a spray-drying method[12] was employed as the active material to explore the kinetics performances

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of $Li_4Ti_5O_{12}$ on different current collectors. The $Li_4Ti_5O_{12}$ electrode was prepared by mixing active material $Li_4Ti_5O_{12}$, carbon black and polyvinylidene fluoride with a proportion of 8:1:1. The slurry was pasted on pure Cu foil, graphite felt and Al foil separately, and then dried at 100 °C in vacuum for 10 h. More detailed information may be found in Ref. [13]. The coin cells were assembled with $Li_4Ti_5O_{12}$ as the working electrode, pure lithium foil as the counter electrode, a glass fibre as the separator, and 1 M $LiPF_6$ EC:DMC (1:1) as electrolyte in an argon-filled glove box. The discharge/charge measurements were carried out in a voltage range between 1.0 and 2.2 V. Electrochemical impedance spectrum (EIS) for the $Li_4Ti_5O_{12}$ electrodes on Cu and Al foils was measured on a Zahner Zennium electrochemical workstation, employing a three-electrode system with pure lithium foil as both the counter electrode and reference electrode. In order to further study the interface effect, the atomic layer deposition (ALD) approach was used to modify the surface of Cu current collector.

3. Results and discussion

To compare the effects of different current collectors on electron transfer, we adopted the same experimental parameters and conditions except for current collectors. Figure 1(a) shows the comparisons of the rate performance among the same $Li_4Ti_5O_{12}$ pasted separately on pure Cu foil, graphite felt and Al foil. It can be obviously seen that the rate performances for $Li_4Ti_5O_{12}$ pasted separately on Cu foil and on graphite felt are similar, but significantly different from that on Al foil.[13] In this study, we focus on Cu and Al current collectors to discuss the critical kinetics of the $Li_4Ti_5O_{12}$. At a low discharge/charge current rate of 0.5 C (Note that 0.5 C means 3 Li insertion into $Li_4Ti_5O_{12}$ in 2 h), the capacity of the $Li_4Ti_5O_{12}$ pasted on either Cu or Al current collector shows little difference (165 $mA{\cdot}h{\cdot}g^{-1}$). While with the increasing current rates, the difference in rate performance between $Li_4Ti_5O_{12}$ pasted on Cu foil and on Al foil becomes more and more obvious. Particularly, at a current rate of 10 C, the $Li_4Ti_5O_{12}$ pasted on Cu foil shows a capacity of 144 $mA{\cdot}h{\cdot}g^{-1}$, about 7 times more than that on Al foil, which is even higher than that of conductive layer coated $Li_4Ti_5O_{12}$ pasted on Al foil reported previously.[9,12] In addition, Figure 1(b) shows that the $Li_4Ti_5O_{12}$ employing Cu foil as current collector also exhibits appealing cycling performance compared with that on Al foil, with an excellent capacity retention of 97% at a current rate of 2 C after 1200 cycles, which indicates that the kinetics between the Cu foil and the $Li_4Ti_5O_{12}$ is not only rapid, but also very stable. The main difference between the above two $Li_4Ti_5O_{12}$ electrodes is the electron transfer between $Li_4Ti_5O_{12}$ and Cu or Al foil. It has been considered that the $Li_4Ti_5O_{12}$ with poor electronic conductivity could not deliver satisfactory rate performance. However, the $Li_4Ti_5O_{12}$ with poor electronic conductivity pasted on Cu foil can also show excellent rate performance, even better than the conductive layer coated $Li_4Ti_5O_{12}$ pasted on Al foil, which should arouse important reconsideration of the effects on the rate performance of this material.

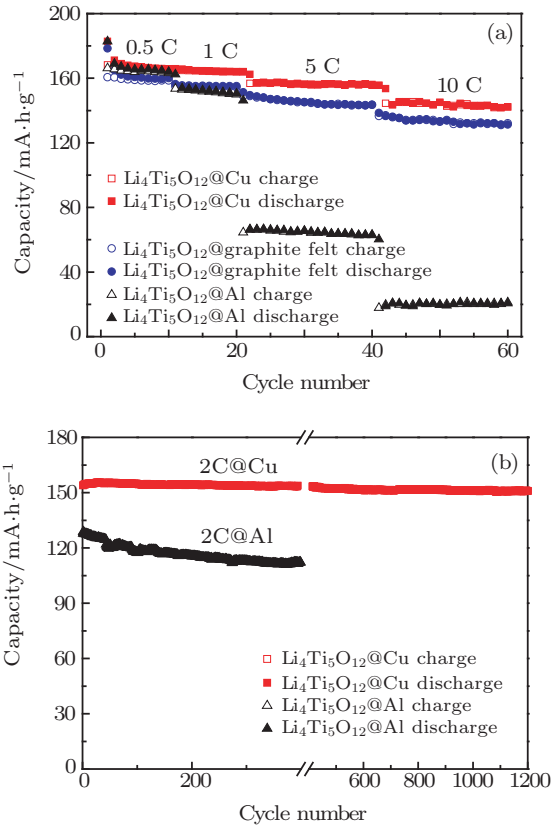


Fig. 1. (colour online) (a) Comparison of the rate performance among $Li_4Ti_5O_{12}$ employing Cu foil, graphite felt and Al foil as current collectors. (b) Comparison of the cycling performance between $Li_4Ti_5O_{12}$ on Cu and Al foils.

There is always Al_2O_3 insulated ultrathin layer on Al foil, which could influence the electron transfer between the current collector and the active material $Li_4Ti_5O_{12}$. In order to explore the reason why the rate capabilities of the $Li_4Ti_5O_{12}$ pasted separately on Cu and Al foils are different, we carried out the comparative experiments: 2 nm and 5 nm Al_2O_3 layers were deposited separately on Cu foil by ALD technique, and then the $Li_4Ti_5O_{12}$ was pasted on Al_2O_3

coated Cu foil, denoted as Sample A-1 (Cu-2 nm Al_2O_3-$Li_4Ti_5O_{12}$) and Sample A-2 (Cu-5 nm Al_2O_3-$Li_4Ti_5O_{12}$) respectively. Figure 2 shows the comparison of the rate performance between the $Li_4Ti_5O_{12}$ electrodes employing Al_2O_3 coated Cu foil as current collectors. The rate capabilities of the modified $Li_4Ti_5O_{12}$ electrodes were both degraded compared with that of the $Li_4Ti_5O_{12}$ on Cu foil. Sample A-1 shows nearly the same rate performance as the $Li_4Ti_5O_{12}$ employing Al foil as the current collector. With the increase of the thickness of the Al_2O_3 layer on Cu foil, the rate performance of the $Li_4Ti_5O_{12}$ becomes worse than that on Al foil, especially at high current rates. That is because the Al_2O_3 layer on Cu foil increases the electron transfer barrier between the current collector and $Li_4Ti_5O_{12}$, indicating that the electron transfer between the current collector and the $Li_4Ti_5O_{12}$ is the limiting step during its electrochemical reactions.

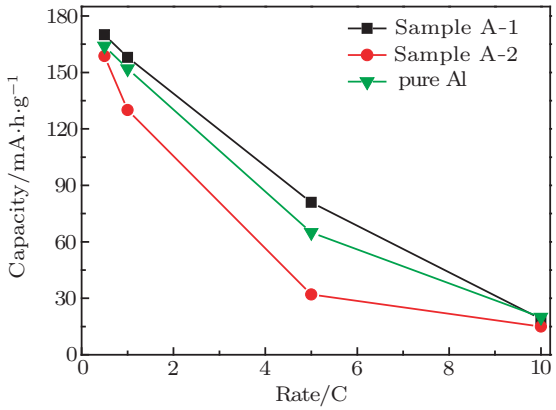


Fig. 2. (colour online) Rate performances of the $Li_4Ti_5O_{12}$ on Cu current collectors coated by Al_2O_3.

It is known that the conductivity of Cu foil is higher than that of Al foil. In addition, there is always an oxidation layer with the thickness of several nanometers, like electronic conductive Cu_2O and insulated Al_2O_3, existing on the surfaces of Cu and Al foils respectively.[14–16] EIS was measured to investigate the kinetics of $Li_4Ti_5O_{12}$ on different current collectors. Figure 3 shows the EIS for $Li_4Ti_5O_{12}$ after one cycle on Cu and Al foils respectively. It can be seen that EIS include a semicircle in the high frequency range and an inclined line in the low frequency range, which could correspond to charge transfer and Warburg impedance respectively.[17] It can be seen that the overall charge transfer resistance of $Li_4Ti_5O_{12}$ on Cu foil is markedly smaller than that of $Li_4Ti_5O_{12}$ on Al foil. The charge transfer process should include the Li^+ transfer in the interface between active material and liquid electrolyte and the electron transfer through the interface between current collector and active material. For both cases, the former should be the same. The difference lies in the electron transfer, which could be one of the important reasons for the different rate performances of the $Li_4Ti_5O_{12}$ on Cu and Al foils.

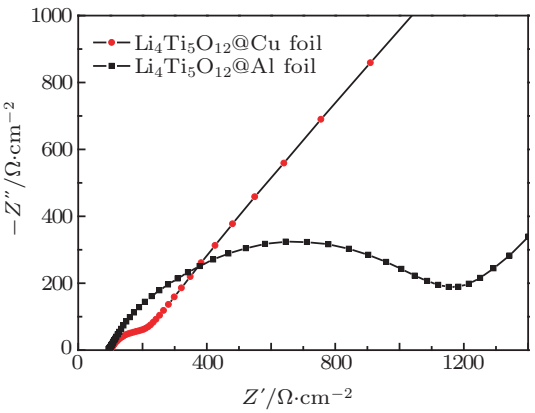


Fig. 3. (colour online) EIS of the $Li_4Ti_5O_{12}$ on Cu and Al foils.

To further understand the difference in kinetics between the $Li_4Ti_5O_{12}$ on Cu foil and on Al foil, we carried out another comparative experiment. Commercial nano-sized anatase TiO_2 was employed to see whether it would also exhibit significantly different rate capabilities when different current collectors were used. The electrodes were prepared with the same experimental parameters as those in the $Li_4Ti_5O_{12}$. It can be seen in Figure 4 that TiO_2 exhibits similar rate performances on Cu and Al foils. For the TiO_2, the electron transfer between the current collector and TiO_2 is not the limiting process during the electrode process, but the low Li^+ diffusion coefficient in TiO_2 (3.8×10^{-15} $cm^2 \cdot s^{-1}$)[18] is the limiting step. That is the reason why TiO_2 shows similar rate performances for both employing Cu and Al foils as current collectors. While for the $Li_4Ti_5O_{12}$, the electronic conductivity of $Li_4Ti_5O_{12}$ is significantly improved after inserting a very small amount of Li[19] and the Li diffusion coefficient in $Li_4Ti_5O_{12}$ is also high (10^{-8}–10^{-9} $cm^2 \cdot s^{-1}$).[20] Therefore, the rate determined step for the $Li_4Ti_5O_{12}$ could be the electron transfer between the current collector and $Li_4Ti_5O_{12}$. Different from Cu foil and graphite felt, for Al foil, the ultrathin Al_2O_3 layer on the Al foil is electronically insulating, electron can only tunnel through the Al_2O_3 surface layer. Electron tunneling probability reduces exponentially with the increases of barrier height and width.[21,22] Particularly, at high current rate, the electron transfer through the Al_2O_3 layer on Al foil cannot follow the speed of reaction, thus

the storage capacity of the $Li_4Ti_5O_{12}$ on Al foil reduces greatly due to kinetic limitation. This is the most important reason why the rate performances of the $Li_4Ti_5O_{12}$ on Cu foil and graphite felt are much superior to that on Al foil.

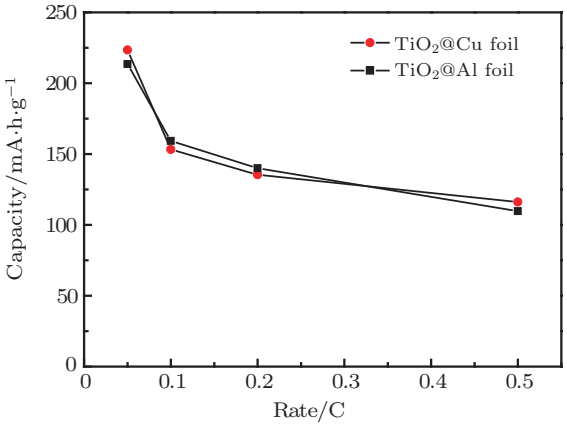


Fig. 4. (colour online) Effect of current collectors on the rate performance of the nano-sized anatase TiO_2.

4. Conclusion

In this study, we show that the rate performance of $Li_4Ti_5O_{12}$ is greatly affected by the used current collectors. The $Li_4Ti_5O_{12}$ employing Cu foil or graphite felt as current collector shows superior rate performance. The highly electronically insulating Al_2O_3 ultrathin layer on Al foil current collector increases the electron transfer barrier, resulting in a poor rate performance for the $Li_4Ti_5O_{12}$. Our comparative experimental results indicate that the electron transfer through the interface between the current collector and the $Li_4Ti_5O_{12}$ is the limiting step in the electrochemical reactions. This unexpected finding will have an important application in the high power Li-ion batteries.

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