



Enhanced high-temperature cycle performance of LiFePO₄/carbon batteries by an ion-sieving metal coating on negative electrode

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ABSTRACT

LiFePO₄/mesocarbon microbead (MCMB) cells of which the carbon electrodes were, respectively, coated with different metal layers were characterized for their charge/discharge cycle performance at 55 °C. The examined metals included Au, Cu, Fe, Ni, Co, and Ti, and the superficial layers were 30–50 nm in thickness and deposited by vacuum sputtering. It was found that the presence of a either Au or Cu layer remarkably reduces capacity fading, while the rest metals only accelerate fading. There was observed a consistent trend between the capacity fading rate and the amount of the solid-electrolyte-interphase (SEI) deposition; the faster the capacity fading, the greater amount of SEI materials appearing on the surface of cycled carbon electrode. Microscopic and composition analyses indicates that the superficial Au and Cu layers act as a sieve to collect the Fe ions that result from erosion of LiFePO₄ before they diffuse into the interior of the carbon electrode, and that the so-deposited Fe particles do not show the tendency to catalyze the SEI formation, as in contrast to those directly deposited on the carbon surfaces.

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1. Introduction

LiFePO₄ has drawn intensive attention in recent years as a promising positive electrode material for high-power Li-ion secondary batteries. Compared with other positive electrode materials, LiFePO₄ has the advantages of high theoretical capacity (170 mAh/g), low toxicity, low cost and excellent thermal safety [1–6], which are important properties for the electric-vehicle (EV) applications [7]. While having demonstrated high-power capability in several studies [8–13], LiFePO₄/carbon (graphite) secondary batteries are known to exhibit fast capacity fading at elevated temperatures, which is foreseen to seriously hamper their usage for EV applications. For instance, Amine et al. [14] have revealed that, although the LiFePO₄/mesocarbon microbead (MCMB) cell has shown a cycle performance with almost no capacity fading after 100 cycles at room temperature, the cells cycled at 37 and 55 °C show capacity fading by 41% and 70%, respectively. The accelerated fading at high-temperatures was attributed to dissolution of Fe from the LiFePO₄ electrode and subsequent deposition of the Fe ions on the carbon electrode, where the metal deposit tends to catalyze the formation of the solid-electrolyte-interphase (SEI) layer. The formation of the SEI layer consumes Li-ions and imposes high surface resistance. Both lead to capacity fading.

Progress in coping with the high-temperature fading problem of the LiFePO₄/carbon (graphite) cells has been scarce except that Wu et al. [15] once showed that by adding vinylene carbonate in the electrolyte, the amount of Fe dissolved was reduced. Amine et al. suggested to replace the carbon (graphite) electrode with Li₄Ti₅O₁₂ [14], which has a higher anode reduction potential (~1.5 V versus Li/Li⁺) so as to avoid SEI formation. While the cycle life is effectively prolonged, the operating voltage window is unfortunately reduced to ~2 V.

In this study, it is demonstrated that the cycle performance of LiFePO₄/carbon cell can be significantly improved by simply depositing a thin layer of appropriate metals, such as Cu and Au, on the carbon electrode. Experimental results showed that this thin metal layer can act as a “sieve” to collect Fe ions during charge/discharge cycling, and that the deposited Fe on the sieving layer appears no longer capable of catalyzing SEI formation, resulting in remarkably reducing capacity fading.

2. Experimental

Commercial LiFePO₄ powder received from Phostech Company was used as the positive electrode material. The powder had a particle size of $d_{50} = 3.0 \mu\text{m}$. The electrode was made of 85 wt.% LiFePO₄, 5 wt.% graphitic flakes (KS6, 3 μm , TIMCAL), 2% nano-sized carbon black (Super P, 40 nm, TIMCAL) and 8 wt.% PVdF (polyvinylidene difluoride; Aldrich), with Al foil as the current collector. For the negative electrode, it contained 93% MCMB (#1028, Osaka Gas)

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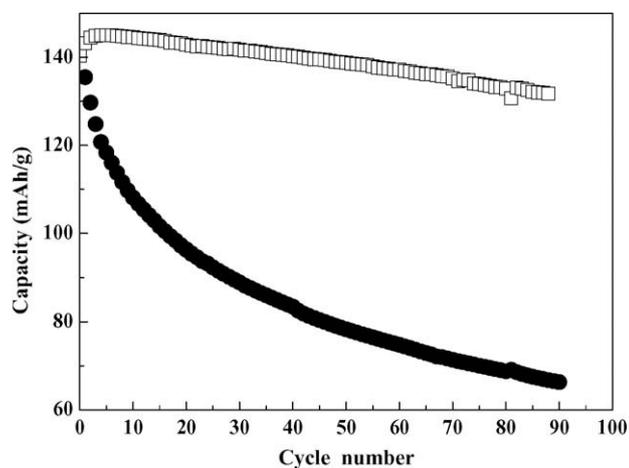


Fig. 1. Cycle performance of LiFePO₄/Li (□) and LiFePO₄/MCMB (●) cells at 55 °C.

and 7% PVdF on Cu foil. To make the metal coated negative electrode, MCMB electrode was put in an ultrahigh vacuum (UHV) sputtering machine. The chamber was evacuated to 10^{-8} mbar and then Ar was refilled to 5 m torr. A metal selected from Au, Cu, Fe, Co, Ni, and Ti was then sputtered onto the electrode surface under the conditions of 280 V and 0.06 A. The metal layers have a thickness in the range of 30–50 nm. The electrodes were assembled into CR2032 coin cells contain electrolyte of 1 M LiPF₆ in a 1:2 v/v mixture of ethylene carbonate and ethyl methyl carbonate (Mitsubishi Chemicals). The assembling process was conducted in a dry room where the dew point was maintained at between –40 and –45 °C. For the charge/discharge tests, the cells were first charged and discharged at 0.1 C rate at room temperature between 2.5 and 4.0 V during the first cycle and then at 1 C–1 C rates for the subsequent cycles at 55 °C over the same voltage window on a charge–discharge tester (Arbin, model: MCN6410).

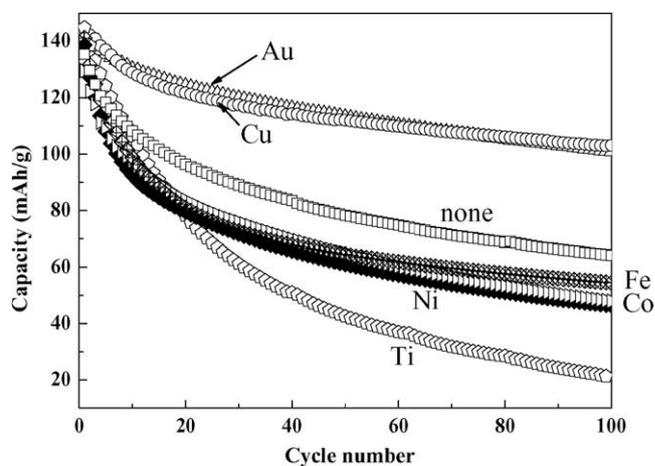


Fig. 2. Cycle performance of LiFePO₄/MCMB cells with different metal coatings, including Au, Cu, Fe, Co, Ni, and Ti, on the MCMB electrode surface. All the cells were cycled at 1 C charge/discharge rate at 55 °C in the voltage window of 2.5–4.0 V.

To prepare samples for surface analyses, the cycled coin cells were disassembled in a glove box under Ar atmosphere, and the electrodes were rinsed with diethyl carbonate (DEC) and dried and stored in the glove box before analysis. Surface and particle morphology were examined by scanning electron microscopy (SEM; LEO1530 and JOEL JSM-6700F). Energy dispersive X-ray spectroscopy (EDX, Oxford Instrument, model: 6587) was used to analyze the compositions of electrodes.

3. Results and discussion

Fig. 1 compares the discharge capacity data of LiFePO₄/Li (the so-called half-cell configuration) and LiFePO₄/MCMB (full-cell) cells at 55 °C. The LiFePO₄/Li cell exhibited a maximum capacity

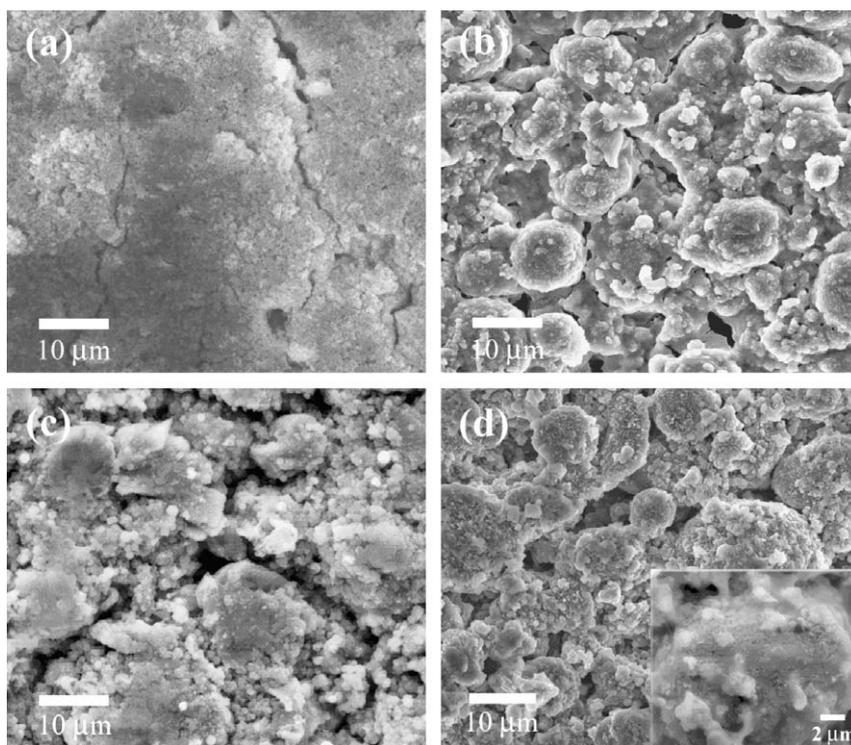


Fig. 3. Surface morphologies of the cycled carbon electrodes with different metal coatings, including (a) Ti; (b) Co; (c) none and (d) Au. The bright nodules appearing on the particle shown in the inset of (d) are Fe-rich.

of 145 mAh/g and a capacity loss of 13 mAh/g after 90 cycles. The LiFePO₄/MCMB cell also had a maximum capacity of 145 mAh/g but exhibited a capacity loss of 79 mAh/g. The capacity loss has increased by ~6 folds. The data, consistent with Amine et al. [14], illustrate the profound capacity fading associated with the use of the carbon negative electrode, presumably due to the accelerated SEI formation processes at the carbon electrode by the superficial Fe deposit, as described earlier.

Fig. 2 summarizes the capacity data for the LiFePO₄/MCMB cells in which the surfaces of carbon electrodes have been deposited with a thin metal layer by using a sputtering technique. For comparison, the data of the cell without any metal coating, i.e., the pristine cell, are also shown. All the cells have about the same initial capacity of ~145 mAh/g, but exhibit rather different fading rate upon cycling. They can be divided into two groups, based on their capacity fading rate relative to that of the pristine cell. One group includes the cells with Au- and Cu-coating, which show remarkably reducing fading. The other group includes the cells with Fe-, Ni-, Co-, or Ti-coating, which exhibit much faster fading rate than the pristine cell. Within the second group, Ti on the carbon electrode is far more detrimental than the other metals in accelerating capacity fading.

SEM analysis of the surfaces of carbon electrodes shows a consistent trend between the capacity fading rate and the amount of

the SEI deposition; the higher the fading rate, the greater amount of SEI materials appearing on the cycled surface of carbon electrode. Fig. 3, for example, compares the surface morphologies of the carbon electrodes corresponding to four distinct fading rates. The Ti-coated carbon electrode (Fig. 3a), of which the cell shows the fastest capacity fading, apparently has the most abundance of SEI deposition. Its surface is covered with a thick SEI layer so that the granular MCMB particles underneath can no longer be seen. The Co-coated carbon electrode (Fig. 3b) has an amount of SEI layer in between those on the Ti-coated and pristine carbon electrodes. While a continuous SEI film is formed in this case, the granular MCMB particles can partially be seen. On the pristine carbon electrode (Fig. 3c), SEI layer was formed on individual MCMB particles, along with additional smaller particles of SEI materials randomly deposited in between the MCMB particles. The Au-coated carbon electrode clearly shows the least amount of SEI formation (Fig. 3d), and the corresponding cell exhibits the least fading rate as described above.

The fact that the Fe-coated carbon electrode shows a faster capacity fading than the pristine cell is consistent with the notion that Fe deposition on the surface of carbon electrode is capable of accelerating SEI formation and hence capacity fading. The detrimental effects by the Ni and Co deposition are consistent with the literature [16,17]. The dramatic adverse effect by the Ti depo-

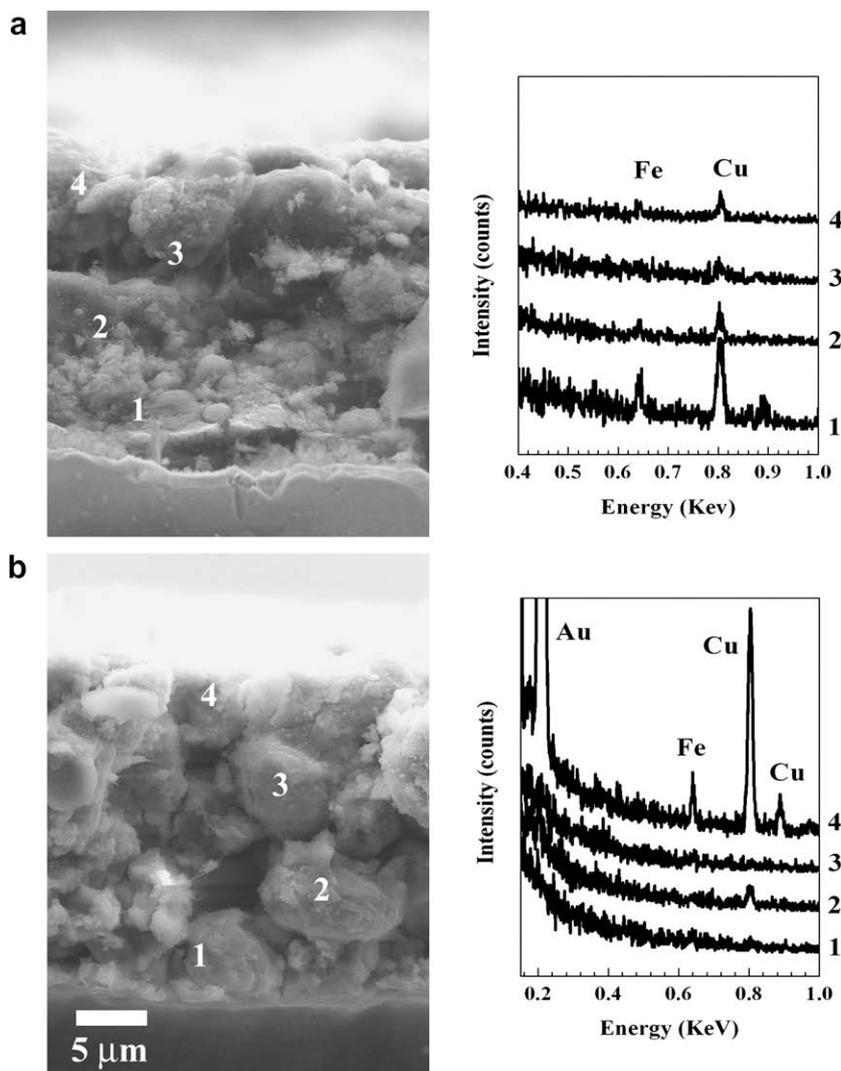


Fig. 4. Cross-sectional SEM images and EDX spectra of (a) pristine and (b) Au-coated MCMB electrodes. The numbers in each figure index the locations where the spectra are acquired.

sition has previously been reported by us, and it has been considered to be the main cause to the capacity fading using TiO₂-coated LiFePO₄ positive electrode [18], where Ti is dissolved from positive electrode and subsequently reduced at the surface of carbon electrode. In contrast, the positive effect by the Au and Cu deposition is unprecedented.

It is interesting to note that EDX analysis conducted laterally on the surfaces of the Au- and Cu-coated negative electrodes still detected significant amount Fe, in spite of remarkably reduced fading rates of the cells. Analysis on the cross-section of the carbon electrodes, however, showed very different Fe distributions between these electrodes and the pristine one. For example, Fig. 4a and b shows the cross-section SEM micrographs and EDX data of the pristine and Au-coated carbon electrodes, respectively. In either micrograph, the top side of electrode is the surface in contact with separator in the cell, while the bottom is the surface binding with copper current collector (the Au-coated carbon electrode was accidentally peeled off from the Cu collector during SEM sample preparation). EDX was carried out in spot-mode along the cross-section at four different locations for each sample. It was found that, for the pristine cell, Fe was detected throughout the cross-section of the electrode, and its concentration increases as getting more into the electrode toward the Cu collector. In contrast, for the Au-coated carbon electrode, Fe was detected in conjunction with Au only near the surface that in contact with separator of the cell. The Fe signal detected from the top layer has a much stronger intensity than any of the Fe signal acquired from the pristine carbon electrode, suggesting that Fe was indeed concentrated within this top layer. It is also noticed that other metal deposits, mainly Cu and Al, which are presumably dissolved from the current collectors and reduced at negative electrode, also show similar trends. Consequently, the Au-coating, as well as the Cu-coating (not shown), seems to behave as a “sieving layer” to sieve out the metal ions before they can diffuse into the interior of the negative electrode layer.

Another interesting fact is that, in spite of concentrated Fe on the surfaces of the Au- and Cu-coated carbon electrodes, the amount of the SEI deposition on these electrodes are the least. On the Au-coated electrode, for instance, Fe was deposited as small nodules on the MCMB surfaces (inset in Fig. 3d), and there is no particular excess SEI accumulation around these nodules. It is inferred that the Fe particles are not intrinsically active in reacting

with the electrolyte to accelerate SEI formation, but active in catalyzing the process only when in direct contact with the C surfaces, where lithiation takes place. As a result, by collecting the Fe ions on the top of the superficial Au and Cu layers, it is possible to reduce overall amount of SEI formation and hence to reduce capacity fading.

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