

# Synthesis and electrochemical characterization of LiFePO<sub>4</sub>/C-polypyrrole composite prepared by a simple chemical vapor deposition method

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**Abstract** A LiFePO<sub>4</sub>/C-polypyrrole (LiFePO<sub>4</sub>/C-PPy) composite as a high-performance cathode material is successfully prepared through a simple chemical vapor deposition (CVD) method. According to the transmission electron microscope (TEM) analysis, the surface of the LiFePO<sub>4</sub>/C is surrounded with PPy in the LiFePO<sub>4</sub>/C-PPy composite. The as-prepared LiFePO<sub>4</sub>/C-PPy material shows outstanding rate capability at 20°C and good cycle performance at 55°C in comparison with those of the bare LiFePO<sub>4</sub>/C material against Li anode. After 700 cycles, the discharge capacity of LiFePO<sub>4</sub>/C-PPy could still remain 110 mA hg<sup>-1</sup> with the retention of 82% at 5 C rate at 55°C. This could be ascribed to the fact that PPy coating on LiFePO<sub>4</sub>/C could significantly improve the ionic conductivity of the LiFePO<sub>4</sub>/C-PPy composite and could greatly reduce the electrode resistance. Furthermore, the PPy coating on LiFePO<sub>4</sub>/C could effectively decrease the dissolution of Fe in the LiPF<sub>6</sub> electrolyte and subsequently suppress the reduction of Fe ions on anode.

**Keywords** LiFePO<sub>4</sub> · Polypyrrole · Chemical vapor deposition · Cathode · Lithium batteries

## Introduction

As a rare metal-free material, LiFePO<sub>4</sub> has been considered a promising cathode material for the next generation of rechargeable lithium ion batteries due to its reasonable theoretical capacity (170 mA hg<sup>-1</sup>), low cost, and high safety, and because it is environmentally benign [1]. However, the main problem of LiFePO<sub>4</sub> is its poor lithium-ion diffusion rate and low electronic conductivity. Tremendous efforts have been made over the past few years to overcome these drawbacks, such as carbon coating [2–4], metal doping [5, 6] and particle size nanonization [7, 8]. Nevertheless, the cycling performance of LiFePO<sub>4</sub> at elevated temperatures and its high rate performance are still unable to satisfy the requirements for practical application in electric vehicles.

In recent years, conducting polymers, such as PPy, polyaniline (PANI), and poly (3,4-ethylenedioxythiophene) (PEDOT), have been attracting much attention as additives or coating materials for lithium ion batteries. Investigations on V<sub>2</sub>O<sub>5</sub>/PPy [9], LiMn<sub>2</sub>O<sub>4</sub>/PPy [10], LiFePO<sub>4</sub>/PEDOT [11], LiFePO<sub>4</sub>/PANI [12], and LiFePO<sub>4</sub>/PPy [12–19] have been reported. Pasquier et al. [10] have coated LiMn<sub>2</sub>O<sub>4</sub> particles with PPy to improve the cyclability of LiMn<sub>2</sub>O<sub>4</sub> cathode at elevated temperatures by suppressing the dissolution of Mn in the LiPF<sub>6</sub> electrolyte. Goodenough et al. [12–15] first presented a concept of substituting the inactive C and PTFE binder of the LiFePO<sub>4</sub> cathode with a conducting polymer like PPy or PANI. The synthesized LiFePO<sub>4</sub>/C-PPy and LiFePO<sub>4</sub>/C-PANI cathodes exhibited excellent rate capability. But they did not report the electrochemical performance of these materials at high temperatures.

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Vapor phase polymerization (VPP) was first described by Mohammadi et al. [20] as a chemical vapor deposition (CVD) process using  $\text{FeCl}_3$  as oxidants for polymerization of polypyrrole films. Then the use of Fe(III) tosylate as oxidant has been reported as an excellent route to form both smooth and highly conducting films [21]. When electrode materials are coated by PPy in this vapor phase process, the pyrrole gas could penetrate and coat in the inner pore area of the powder. This would reduce the activity of cathode/anode surface and further decrease undesirable reactions with the electrolyte, while the lithium intercalation would not be inhibited. This strategy to synthesize the PPy films grown on the surface of  $\text{LiFePO}_4$  with CVD procedure would be helpful for the further development of electrode material for lithium ion batteries.

In this report, the effect of PPy coating on the rate capability of  $\text{LiFePO}_4/\text{C}$  material is first investigated at low temperature ( $-20^\circ\text{C}$ ). We also demonstrate that the high-temperature cycle performance of the  $\text{LiFePO}_4/\text{C}$  material can be greatly enhanced with the coating of PPy by using the simple CVD method regardless of whether the counter electrode is metallic lithium or mesocarbon microbead (MCMB).

## Experimental

$\text{LiFePO}_4/\text{C}$  powder with carbon content of 2.4 wt.% was synthesized according to the method described by Wang et al. [22].  $\text{LiFePO}_4/\text{C}$ -PPy composite was prepared via the CVD method using Fe(III) tosylate as oxidant: 5 g  $\text{LiFePO}_4/\text{C}$  powder was dispersed in 23.5 g ethanol solution containing 25 wt.% Fe(III) tosylate (Sigma-Aldrich). The solution was magnetically stirred for 15 min and heated into slurry at  $60^\circ\text{C}$ . Then the slurry was exposed to pyrrole monomer vapor directly over the liquid pyrrole monomer (98%, Sigma-Aldrich, distilled prior to usage) on a filter paper in a sealed container at  $60^\circ\text{C}$  for 1 h. The final  $\text{LiFePO}_4/\text{C}$ -PPy product was washed with ethanol, and dried at  $60^\circ\text{C}$  in a vacuum oven for 2 h.

The PPy content in the composite was analyzed by thermogravimetric analysis (NETZSCH TG 209 F1) operated under flowing Ar. The temperature was scanned from  $30^\circ\text{C}$  to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  using an  $\text{Al}_2\text{O}_3$  crucible. The particle images of the samples were observed using transmission electron microscopy (TEM, JEM-2010/INCA OXFORD). The cross-section morphology of electrodes after cycling was observed using a scanning electron microscope (FESEM, SIRION 200, FEI) at an accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopy (EDX; INCA, Oxford) was used to analyze the compositions of electrodes.

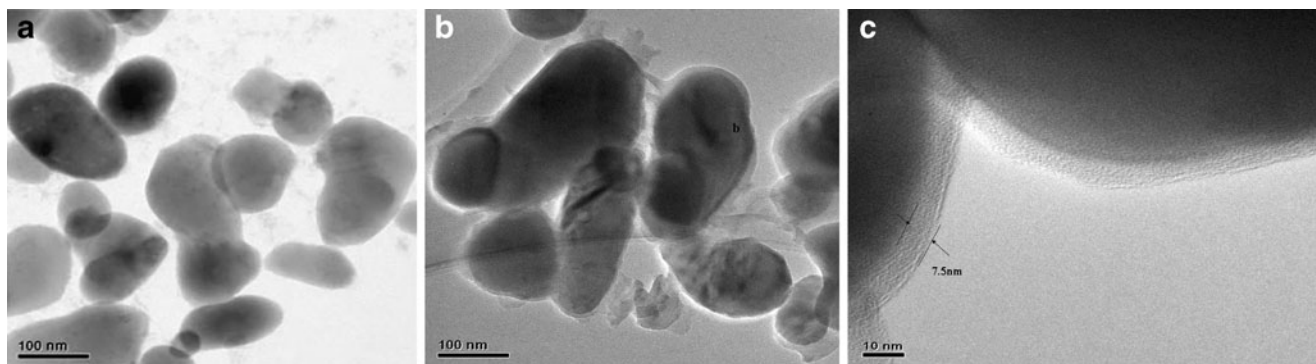
Sample electrodes were prepared by slurring the sample powder with 10 wt.% poly(vinylidene fluoride) (PVDF)

and 15 wt.% Super-P carbon black (Timcal) in *N*-methyl-2-pyrrolidinone (NMP) solvent, and then casting the mixture onto an aluminum foil. After vacuum drying at  $120^\circ\text{C}$  for 8 h, the electrode disks were punched and weighed. The cathodes were incorporated into cells with a lithium foil counter electrode (so-called half-cell configuration), a Celgard<sup>®</sup>-2700 separator, a 1 M  $\text{LiPF}_6$ /ethylene carbonate (EC) + dimethyl carbonate (DMC) + diethyl carbonate (DEC) + ethylmethyl carbonate (EMC) (1:1:1:3, v/v) electrolyte for low temperature ( $-20^\circ\text{C}$ ) and a 1 M  $\text{LiPF}_6$ /DMC + EC (1:1) electrolyte for room temperature ( $20^\circ\text{C}$ ) and high temperature ( $55^\circ\text{C}$ ) test. The active material loaded on the electrode disks was about  $4.5 \text{ mg/cm}^2$ . Galvanostatic charge–discharge cycling tests for the cells were performed within a range of 2.0–4.2 V using a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics Co., Ltd). Parallel tests were made for charge–discharge measurements. The specific capacities of the samples were calculated based on the mass of the composites. Furthermore, the negative electrode in the full-cell test was made of 94% MCMB graphite and 6% PVDF on Cu foil. And the charge/discharge tests of the entire cells were performed at 1 C (1 C =  $160 \text{ mA g}^{-1}$ ) rate between 2.5 and 3.8 V on the same battery test system at  $55^\circ\text{C}$ . Iron dissolution from the sample powders upon storage in the electrolyte was analyzed by an ICAP6300 inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermal, USA). For iron dissolution test, 1 g sample powder was stored in a closed bottle containing 10 ml of electrolyte solution under Ar atmosphere. The bottle was sealed in an aluminum soft package to confirm the completely sealed condition during the long-term test. The solution was removed after 25 days storage at  $55^\circ\text{C}$  and was analyzed.

Electrochemical impedance measurements of the cells were carried out using a SI1260 Impedance/gain-phase analyzer in conjunction with the SI1287 electrochemical interface. The amplitude of the alternating current signal was 5 mV over the frequency range between 100 kHz and 1 mHz.

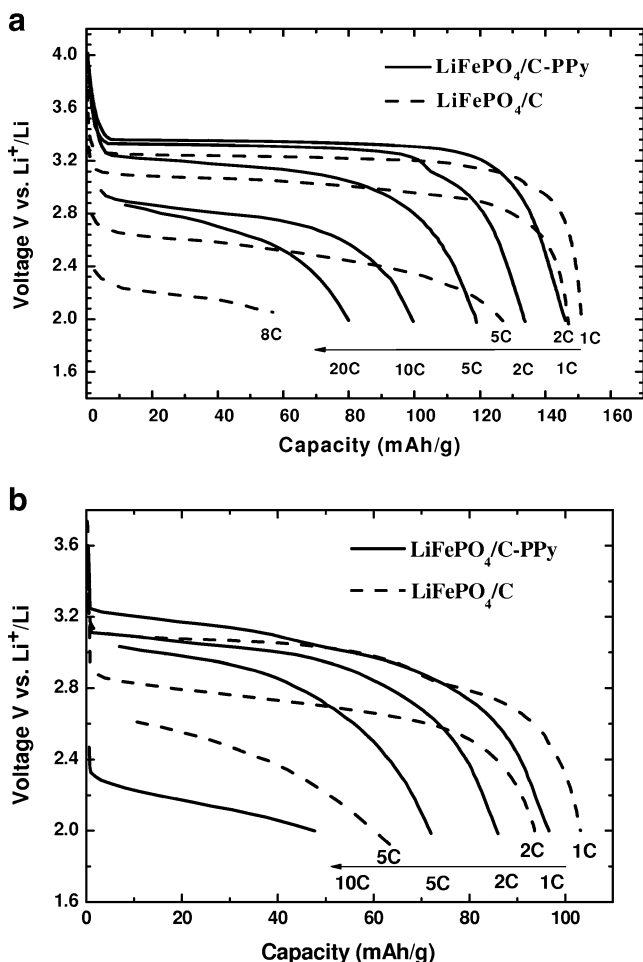
## Results and discussion

Figure 1 shows the TEM images of  $\text{LiFePO}_4/\text{C}$  and  $\text{LiFePO}_4/\text{C}$ -PPy. The surface of  $\text{LiFePO}_4/\text{C}$  particles is very smooth in Fig. 1a. It can be seen in Fig. 1b that there is a large amount of PPy wrapping and connecting the  $\text{LiFePO}_4$  particles. Moreover, the distinct PPy film could be observed on the surface of  $\text{LiFePO}_4$  particles in Fig. 1c. Thus, this could ensure good electrical continuity between  $\text{LiFePO}_4$  particles. The result obtained by TG analysis indicates that the amount of PPy in the  $\text{LiFePO}_4/\text{C}$ -PPy composite was about 11.1 wt.%.



**Fig. 1** TEM images of **a** LiFePO<sub>4</sub>/C and **b, c** LiFePO<sub>4</sub>/C-PPy

The rate capabilities of the prepared LiFePO<sub>4</sub>/C and LiFePO<sub>4</sub>/C-PPy were evaluated and compared at 20°C and -20°C, respectively, as shown in Fig. 2. The cells were charged using the same current density as the following discharge test before each rate capability test. As shown in Fig. 2a, the as-prepared LiFePO<sub>4</sub>/C-PPy composite shows

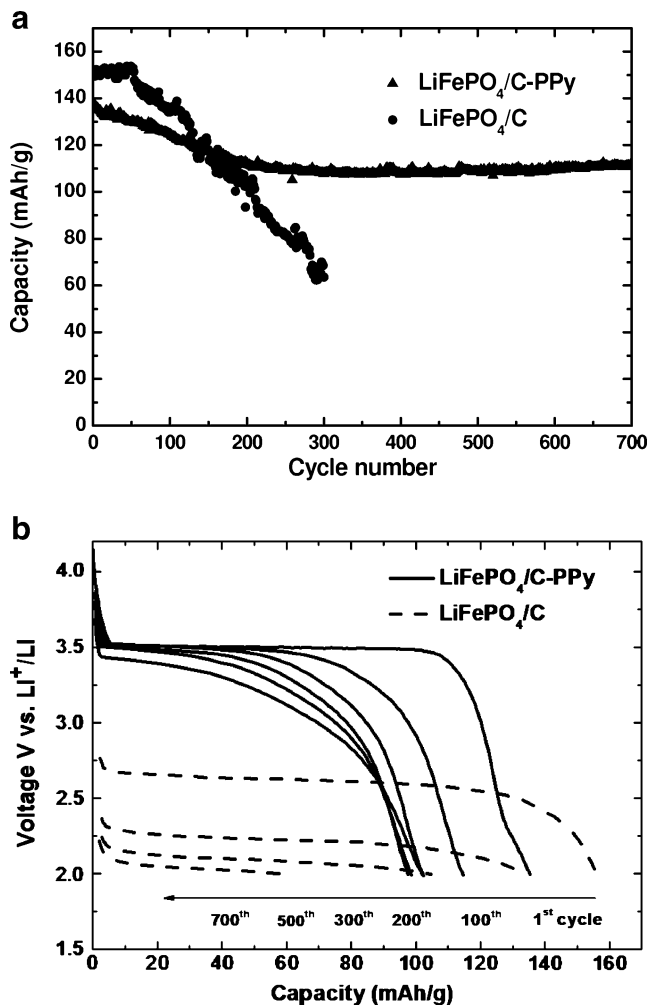


**Fig. 2** Rate capabilities of the Li|LiFePO<sub>4</sub>/C and Li|LiFePO<sub>4</sub>/C-PPy cells at **a** 20°C and **b** -20°C

a superior rate capability over 2 C (320 mA g<sup>-1</sup>) rate, and the overpotential at high discharge rates is significantly reduced in comparison with the pristine LiFePO<sub>4</sub>/C at 20°C. The discharge capacity of LiFePO<sub>4</sub>/C-PPy composite could still remain about 80 mA hg<sup>-1</sup> at 20 C rate. Research on the low temperature performance of the LiFePO<sub>4</sub>/C material is still a challenging requirement. Figure 2b compares the rate capabilities of the LiFePO<sub>4</sub>/C and LiFePO<sub>4</sub>/C-PPy at -20°C. It can be seen that the LiFePO<sub>4</sub>/C-PPy composite does not show an outstanding advantage over the LiFePO<sub>4</sub>/C material, which could be primarily attributed to the poor electronic conductivity of PPy at low temperature. So PPy coating could not noticeably improve the rate capability of LiFePO<sub>4</sub>/C material at low temperature.

As is well known, the poor high-temperature cycling performance of LiFePO<sub>4</sub>/C is a major drawback at high rates. Therefore, the effect of PPy coating on the cycling stability of LiFePO<sub>4</sub>/C material at 55°C is shown in Fig. 3 against Li anode. As shown in Fig. 3a, the LiFePO<sub>4</sub>/C-PPy cathode exhibited excellent high-temperature cycling stability with a first discharge capacity of 135 mA hg<sup>-1</sup>. The steady discharge capacities could be still achieved at 110 mA hg<sup>-1</sup> after 700 cycles, and the capacity retention was about 82%. The initial discharge capacity of the bare LiFePO<sub>4</sub>/C electrode is 149.7 mA hg<sup>-1</sup>. However, the retention value of discharge capacity is only about 40% after 300 cycles. Figure 3b exhibits the discharge profiles of the prepared samples at different cycle numbers. It is clear that the LiFePO<sub>4</sub>/C-PPy cathode displays a relatively stable discharge voltage plateau between about 3.4 and 3.5 V vs. Li<sup>+</sup>/Li during 700 cycles. Nevertheless, the discharge plateau of pristine LiFePO<sub>4</sub>/C is only around 2.6 V at first cycle and drops to around 2.0 V at the 300th cycle.

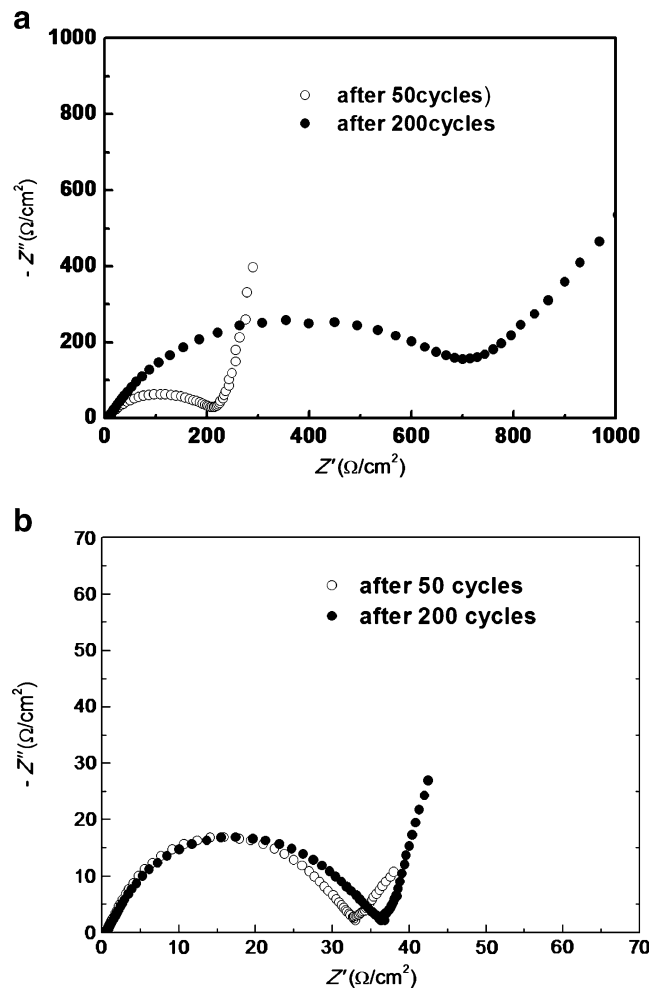
AC electrochemical impedance spectra are taken to understand the effects of PPy coating on the high-rate cycling performance of LiFePO<sub>4</sub>/C electrode at elevated temperature, the AC impedance spectra of Li|LiFePO<sub>4</sub>/C-PPy and Li|LiFePO<sub>4</sub>/C cells were tested after 50th and 200th



**Fig. 3** Cycling performance (a) and discharge curves (b) of Li|LiFePO<sub>4</sub>/C and Li|LiFePO<sub>4</sub>/C-PPy cells at 5 C charge/discharge rate at 55°C

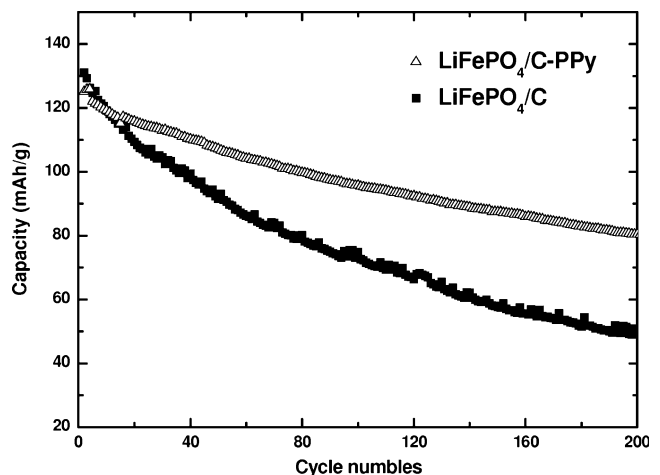
cycles. As shown in Fig. 4, the total interfacial resistance of the Li|LiFePO<sub>4</sub>/C cell, reflected by the high frequency semicircle, was much larger than that of Li|LiFePO<sub>4</sub>/C-PPy cell. Furthermore, the total interfacial resistance of the Li|LiFePO<sub>4</sub>/C cell increased obviously after 200 cycles to three times of that after 50 cycles. In contrast, the total interfacial resistance of Li|LiFePO<sub>4</sub>/C-PPy cell did not change much after 200 cycles. There must be significant changes on the interface of LiFePO<sub>4</sub>/C electrode after long-term cycling.

Figure 5 compares the discharge capacity data of MCMB|LiFePO<sub>4</sub>/C and MCMB|LiFePO<sub>4</sub>/C-PPy cells in full-cell tests at 1 C charge/discharge rate at 55°C. The cycling performance of the MCMB|LiFePO<sub>4</sub>/C-PPy cell is obviously improved in comparison with that of the MCMB|LiFePO<sub>4</sub>/C cell, which is consistent with the result in half-cell test. The aforementioned results indicate that the PPy incorporation plays an important role in the remarkable improvement of the rate capability and cycling performance



**Fig. 4** Impedance spectra for a Li|LiFePO<sub>4</sub>/C cell and b Li|LiFePO<sub>4</sub>/C-PPy cell

of LiFePO<sub>4</sub>/C. It could be attributed to a synergistic effect occurred in LiFePO<sub>4</sub>/C-PPy composite. Firstly, PPy in hybrid material could allow for effective electrolyte



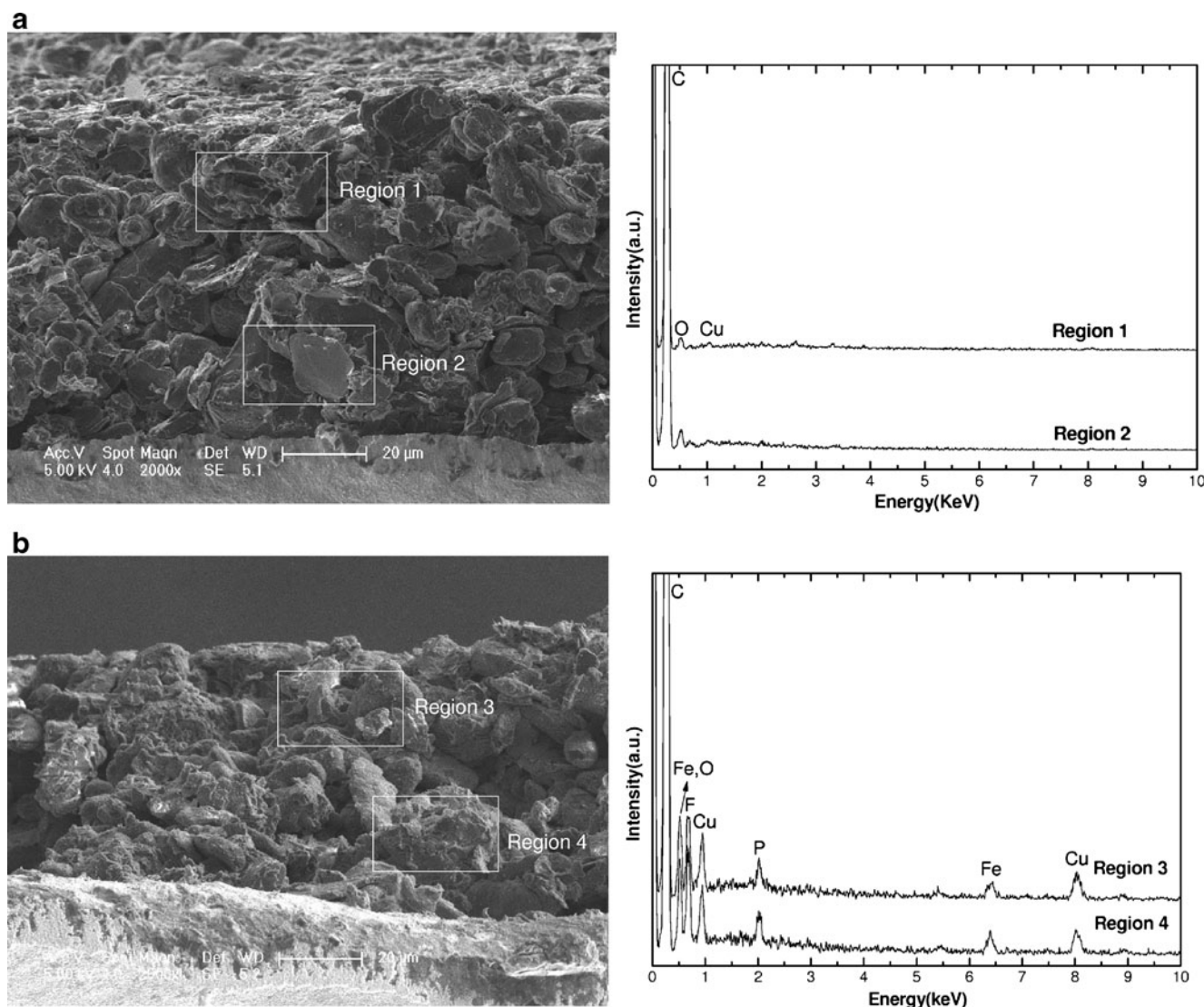
**Fig. 5** Cycling performance of MCMB|LiFePO<sub>4</sub>/C and MCMB|LiFePO<sub>4</sub>/C-PPy cells at 1 C charge/discharge rate at 55°C



penetration into the polymer mass and form a gel-like structure, which could improve the ionic conductivity of the  $\text{LiFePO}_4/\text{C}$ -PPy composite and greatly reduce the electrode resistance [13]. Secondly, in the  $\text{LiFePO}_4/\text{C}$ -PPy composite, the excellent flexibility of PPy polymer could make the electrode more insensitive to the mechanical stresses experienced during cycling at high temperature and high rates [12]. Furthermore, PPy could also contribute to the capacity of the  $\text{LiFePO}_4/\text{C}$ -PPy composite [19].

To further investigate the origin of the remarkable cyclability improvement of the MCMB| $\text{LiFePO}_4/\text{C}$ -PPy cell, the cross-sectional SEM images and the corresponding EDX spectra of MCMB electrodes were measured after 200 cycles at 1 C charge/discharge rate at 55°C. To prepare samples for SEM analysis, the cycled coin cells were disassembled and the MCMB anodes were rinsed with

tetrahydrofuran (THF) and dried in the glove box. EDX was carried out along the cross-section at two different locations for each sample. The results are shown in Fig. 6. Figure 6b shows that, for the MCMB electrode of the MCMB| $\text{LiFePO}_4/\text{C}$  cell, the Fe signal could be clearly detected throughout the cross-section of the electrode. It is also shown that the dissolved  $\text{Fe}^{2+}$  was reduced at the surface of the MCMB electrode. However, for the MCMB electrode of the MCMB| $\text{LiFePO}_4/\text{C}$ -PPy cell, the EDX spectrum (Fig. 6a) indicates that no trace of Fe metal could be detected at the carbon surface. In order to confirm the effects of the PPy coating on iron dissolution, both  $\text{LiFePO}_4/\text{C}$ -PPy and  $\text{LiFePO}_4/\text{C}$  samples were stored in  $\text{LiPF}_6$  solution at 55°C for 25 days. The iron content in the solution after 25 days of storage was  $10 \pm 2$  ppm for  $\text{LiFePO}_4/\text{C}$ -PPy and  $653 \pm 30$  ppm for  $\text{LiFePO}_4/\text{C}$  sample, respectively.



**Fig. 6** Cross-sectional SEM images and EDX spectra of MCMB electrodes after 200 cycles at 1 C charge/discharge rate at 55°C: **a** MCMB| $\text{LiFePO}_4/\text{C}$ -PPy, **b** MCMB| $\text{LiFePO}_4/\text{C}$ . The regions in each figure index the locations where the spectra are acquired

The obtained results (as discussed above) could be attributed to the fact that PPy coating could effectively protect the  $\text{LiFePO}_4/\text{C}$  matrix from the corrosive solution, greatly decrease the dissolution of Fe in the electrolyte at elevated temperature and further suppress the reduction of Fe ions at the carbon electrode at elevated temperature, which is the main reason for the excellent cyclability of  $\text{LiFePO}_4/\text{C}$ -PPy against carbon electrode at elevated temperature [23–25].

## Conclusions

The surface of  $\text{LiFePO}_4/\text{C}$  material is modified with PPy by a simple CVD method. The test results demonstrate that PPy coating could not obviously improve the rate capability of  $\text{LiFePO}_4/\text{C}$  material at low temperature. However, the obtained  $\text{LiFePO}_4/\text{C}$ -PPy composite exhibits excellent rate capability at 20°C and cycle performance at 55°C in comparison with those of the bare  $\text{LiFePO}_4/\text{C}$  material against Li anode. The discharge capacity of  $\text{LiFePO}_4/\text{C}$ -PPy composite could still remain about 80 mA  $\text{hg}^{-1}$  at 20 C rate at 20°C, and the capacity retention of the  $\text{LiFePO}_4/\text{C}$ -PPy composite could still retain 82% at the 700th cycle at 5 C charge–discharge rate at 55°C. The particular structure of  $\text{LiFePO}_4/\text{C}$  particles surrounded by the PPy could improve the ionic conductivity of the  $\text{LiFePO}_4/\text{C}$ -PPy composite and greatly reduce the electrode resistance, which leads to a superior electrochemical performance at room temperature. Moreover, the PPy coating on  $\text{LiFePO}_4/\text{C}$  could effectively decrease the dissolution of Fe in the  $\text{LiPF}_6$  electrolyte and consequently suppress the reduction of Fe ions at the carbon electrode at elevated temperature. Therefore, the surface modification with PPy coating is a promising approach to improve the cycle performance of  $\text{LiFePO}_4/\text{C}$  at high rates and high temperature.

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