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Polymerization of aniline in the interlayer space of molybdenum trioxide and its electrochemical properties

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ABSTRACT

Molybdenum trioxide/polyaniline (MoO_3/PANI) composite was prepared first by ion-exchange reaction between aniline (ANI) and dodecylamine (DDA) which was intercalated precursor, and then was formed under the polymerization of ANI within the interlayer space of MoO_3 at 120 °C for 3 d in air. According to powder X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, infrared spectroscopy and electrochemical testing, MoO_3/PANI composite has layered structure, and its interlayer spacing is 1.127 nm. Moreover, it has high thermal stability with the compound and completes its weight loss at 751.9 °C. Electrochemical investigation shows that MoO_3 is the major active substance in the MoO_3/PANI electrode, and MoO_3/PANI electrode demonstrates better conductivity and electrochemical activity than pure MoO_3 electrode, attributed to the promotion of Li^+ and/or electron transport. In addition, the alternating current impedance proves that if the resistance of MoO_3/PANI electrode reduces apparently, the electrochemical activity will increase correspondingly, the same as the relationship between the ohmic resistance and the electrical conductivity.

1. Introduction

Conductive PANI is considered as the most promising polymer to be used extensively in the future. By nanocompositing with layered compounds, the mechanical properties, stability of interface, thermal stability and processability of PANI will be greatly improved. Besides good conductivity and application perspective in rechargeable cell, this kind of nanocomposites may also have many novel properties, such as photoelectric display, photoelectric transition, thermoelectricity, electromagnetism and elecrorheology through the synergic interaction of PANI with layered compounds [1,2].

In recent years, studies on the properties of the intercalated materials have mainly focused on the electrochemical properties. Both the good electron conductivity, proton conductivity and their synergistic reaction have displayed a lot of new properties, enhancing the importance of the studies on how to apply the composite to electrochemistry [3,4]. The intercalated organic–inorganic materials have widely attracted people's attention in these years [5–8]. Among numerous composite of PANI, MoO_3/PANI composite has caused the greatest concerns as it shows many new features in the lithium battery, the gas sensor, etc. [9–14]. However, MoO_3 does not carry exchangeable ions and its oxidbillity is weak. Consequently, it is difficult to intercalate polymers like PANI into the interlayer space of MoO_3. Since 1993 when Rabin Bissessur and others initially intercalated PANI into the interlayer space of MoO_3 [15], people have been making efforts to find an easy and effective way to prepare the layered MoO_3/PANI composite all along [16–19].

Usually, people primarily reduce MoO_3 to $(Li/Na)_xMoO_3$ to expand the space between the interlayers, and then fill them with the exchangeable cations in order to intercalate the ANI monomer or the oligomers. However, it is difficult to prepare the precursor of $(Li/Na)_xMoO_3$ as well as to preserve it, and it can only be used in aqueous solution. Thus, we changed the traditional method of preparation by using DDA as intercalation agent to modify MoO_3 and exchanging it with ANI in the anhydrous acetic acid. Finally, we succeeded in preparing the layered MoO_3/PANI composite with single-layer arrangement of ANI. That is the first step of the in-situ polymerization.

The second step is to use the outside initiators in the polymerization, because of the weak oxidbillity of MoO_3. In this process, people usually choose the initiators like $(NH_4)_2S_2O_8$, $FeCl_3$, etc. as oxidants. However, in the in-situ polymerization, cations in the oxidant are very likely to replace the ANI and occupy the space between the interlayers [21], even may cause the ANI off the interlayers to form a polymer cover and affect the layered structure. Therefore, on the basis of not breaking the layered structure, we effectively caused the ANI between the interlayers to polymerize and form pure layered MoO_3/PANI composite. The PANI chain in this composite exists in parallel with the interlayer space of MoO_3. For the particular conjugated structure of PANI and its highly ordered arrangement between the interlayers, there is an obvious change about electrochemical property of MoO_3 after it combined with PANI.

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2. Experimental

2.1. Preparation

All other reagents are of AR grade from Shanghai Chemical Reagent Company. MoO_3 powder was pre-treated at 600 °C overnight in air prior to use.

The molybdenum oxide/dodecylamine (MoO_3/DDA) composite as the intermediate product was prepared by the literature method [20], and was then used to prepare molybdenum oxide/aniline (MoO_3/ANI) [25]. ANI was intercalated by adding excess ANI (10 mL) to a sonicated suspension of 0.5 g MoO_3/DDA composite in anhydrous acetic acid (50 mL), heated at 70 °C for 7 d. After being filtered, washed with absolute ethanol and grilled at 120 °C for 3 d in air, the molybdenum trioxide/polyaniline (MoO_3/PANI) composite was obtained.

2.2. Analysis

The products were characterized by powder X-ray diffraction (D/Max-2550 XRD, Cu$K\alpha$ radiation). Scanning electron microscopy (SEM) image was obtained with a JEOL JSM-6700F operated at beam energy of 10.0 kV. In addition, infrared spectroscopies were carried out on AVATRA370 IR spectrometer, and thermal analyses (TG–DSC) in N_2 were performed on thermal analysis system (NETZSCH, STA409PC) at a heating rate of 10 °C min^{-1}. The electrochemical property was studied by Solartron brainpower invariable potentiometer.

3. Results and discussion

The structure of MoO_3 consists of vertex-sharing chains of distorted MoO_6 octahedra [22], which share edges with two similar chains to form layers. The two-dimensional bonded double-octahedra oxide sheets are stacked in a layered arrangement and held together by weak Van der Waals forces.

Fig. 1(a) is the XRD pattern of layered MoO_3. From the position of the diffraction peak 0 2 0, we can find out the interlayer spacing (d) is 0.692 nm, which is consistent with the reported value [26]. Fig. 1(b)–(d) are, respectively, the XRD patterns of layered MoO_3/DDA composite, MoO_3/ANI and MoO_3/PANI. At the position where the peak 0 1 0 appears, its interlayer spacing (d) and the free interlayer spacing (Δd) compared with the pure MoO_3 are all included in Table 1. According to Fig. 1(c), after ANI monomer was intercalated, a new strong diffraction peak 0 1 0, whose interlayer spacing is 1.318 nm and free interlayer spacing is 0.626 nm, appeared in a small-angle direction of the XRD pattern of the layered MoO_3/ANI composite compared with the pure layered MoO_3. It is similar to the interlayer spacing when layered ANI molecule is vertical to the inorganic interlayer plate [21]. After ANI polymerized via heat treatment in air, its diffraction peak 0 1 0 moves a short distance in the large-angle direction and the interlayer spacing decreases to 1.127 nm. It is notable that after ANI polymerized in the interlayers, the free interlayer spacing becomes 0.435 nm, which is smaller than the diameter of ANI molecule (0.57 nm). So it is impossible to have a monolayer of the PANI to exist vertically with the inorganic interlayer plate [2,14]. The free interlayer spacing is similar to the MoS_2/PANI composite whose intercalated PANI is in parallel with the inorganic layered plate direction in the interlayers [23]. According to this, we infer that the molecules intercalated into the interlayer space of MoO_3 had turned 90° when triggered by oxygen in air during the polymerization process. That is, the intercalated PANI was parallel with the direction of inorganic layered plate. Fig. 2 is the

Table 1
Interlayer spacing of (a) MoO_3, (b) MoO_3/DDA, (c) MoO_3/ANI, and (d) MoO_3/PANI.

Layered composite	2θ (deg)	d (nm)	Δd (nm)
(a) MoO_3	12.78	0.692	
(b) MoO_3/DDA	2.68	3.086	2.394
(c) MoO_3/ANI	6.70	1.318	0.626
(d) MoO_3/PANI	7.84	1.127	0.435

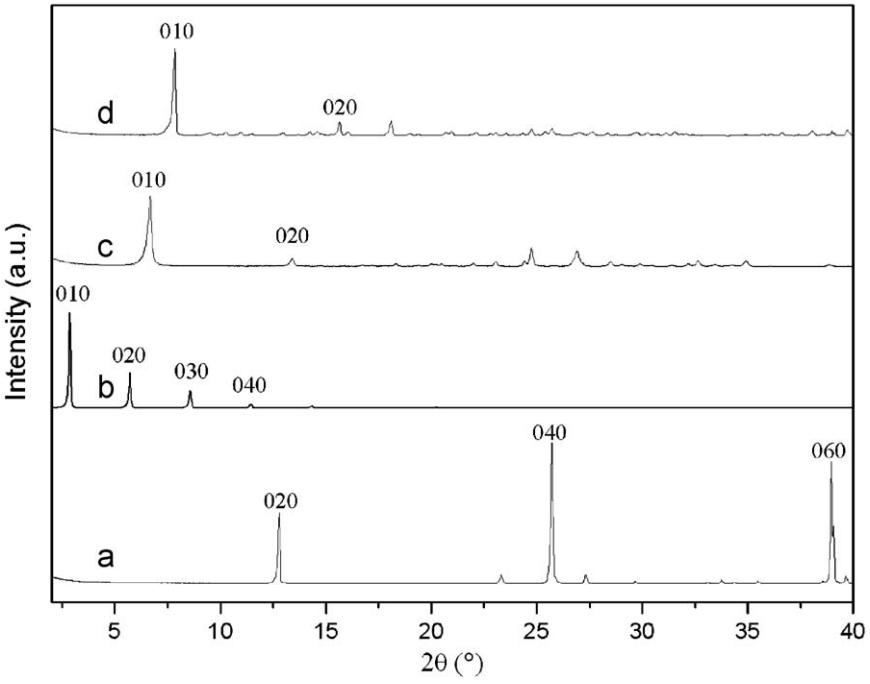

Fig. 1. XRD patterns of layered (a) MoO_3, (b) MoO_3/DDA, (c) MoO_3/ANI, and (d) MoO_3/PANI.

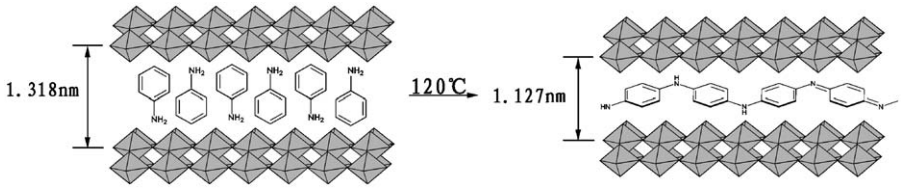

Fig. 2. Schematic presentation of the arrangement of intercalated (a) ANI, and (b) PANI in the interlayer space of MoO_3.

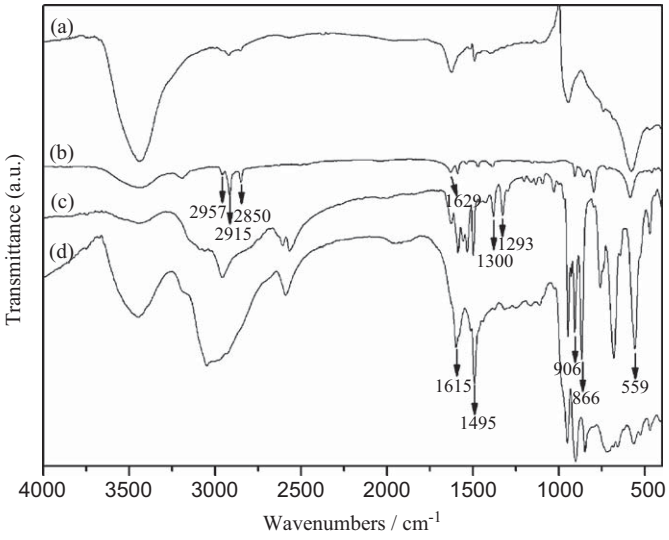

Fig. 3. Infrared spectra of layered (a) MoO_3, (b) MoO_3/DDA, (c) MoO_3/ANI, and (d) MoO_3/PANI.

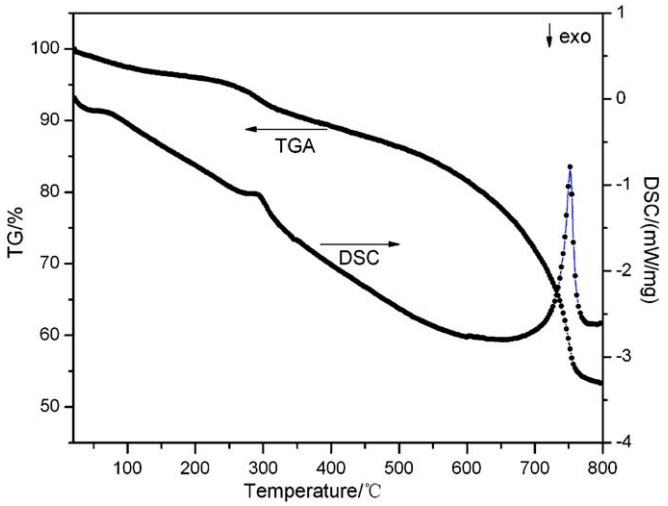

Fig. 4. TG–DSC curves of MoO_3/PANI.

schematic presentation of the arrangement of intercalated (a) ANI and (b) PANI in the interlayer space of MoO_3.

Fig. 3(a)–(d) are, respectively, the infrared spectra of layered MoO_3, MoO_3/DDA, MoO_3/ANI and MoO_3/PANI. Based on the literature value [24], the lattice vibrations of MoO_3 appear at 581, 868, and 994 cm^{-1}. Fig. 3(a) indicates the signals of three bands at 586, 865, and 995 cm^{-1}, which is due to the lattice vibrations of MoO_3. As showed in Fig. 3(b), two bands that appeared at 2851 and 2915 cm^{-1} in the MoO_3/DDA can be attributed to the antisymmetric and symmetric CH_2 stretching vibrations, respectively. Bands corresponding to NH bending vibration are observed at 1629 cm^{-1}. After the ANI was intercalated, Fig. 3(c) shows that the lattice vibrations of MoO_3, respectively, move to 559, 866, and 906 cm^{-1}. In addition, two bands at 1496 and 1615 cm^{-1} in Fig. 3(c) and (d) can be attributed to the stretching vibrations of C=C bond. Bands corresponding to the stretching vibrations of C–N bond are observed at 1293 and 1300 cm^{-1}. All of these characteristic absorption bands prove that the ANI has polymerized in the interlayer space of MoO_3.

Fig. 4 displays the TG–DSC curves of MoO_3/PANI composite under the protection of nitrogen. Corresponding to the literature value [2,10], PANI chain in the whole heat-treatment process is in continuous weight loss, but the weight loss of the composite in literature ranging from 450 to 550 °C is expanded to 751.9 °C here. Thus, the composite has better thermal stability. The TG–DSC curves show that there is a sharp endothermic peak at 751.9 °C, which accords with the main weight loss of PANI. The longer the PANI chain is, the harder it is desorbed by the interlayers. So the composite has an increasing average chain length compared with the MoO_3/PANI composite made by traditional methods. In addition, it is worth noting that: as MoO_3 cannot be decomposed under 800 °C, all the weight loss between 20 and 751.9 °C can be regarded as the weight loss of PANI. On such basis, the content of PANI takes 48% of the whole composite, which is 2–3 times more than the composite made by the traditional methods. For the reason that our method uses air as oxidant the products are less polluted by cation oxidation, thus creating a higher purity and a greater polymerization degree of the MoO_3/PANI composite.

Fig. 5 is the cyclic voltammograms of the MoO_3/PANI electrode and the MoO_3 electrode (containing 15 wt% acetylene black) in 0.5 mol L^{-1} Li_2SO_4 electrolyte. The cyclic scanning ranges from −1.0 to 1.0 V, and the scan rate is 5 mV s^{-1}. Because in MoO_3/PANI composite both PANI and MoO_3 have electrochemical response, their cyclic voltammetry curves are compared and analyzed to have a clearer understanding of the role of PANI in MoO_3/PANI composite.

As is shown in Fig. 5, there are oxidation peaks of both MoO_3/PANI composite and MoO_3 at the vicinity of 0.7 V, which have similar shape. But the oxidation peak current of MoO_3/PANI electrode is stronger. According to the literature [2], MoO_3 and Li^+ can form certain forms of Li^+ intercalated composite in aqueous solution, corresponding to oxidation and reduction processes of the cyclic voltammetry curves. As a result, this whole process mainly manifests itself in the intercalation and de-intercalation of Li^+ in the interlayer space of MoO_3. The oxidation peaks of MoO_3/PANI composite and MoO_3 share similar position at the beginning, that is, MoO_3 is the main electrochemical active substance in MoO_3/PANI composite electrode. In other words, the electrochemical activity of MoO_3/PANI composite is mainly presented in the intercalation and de-intercalation of Li^+ in the interlayer space of MoO_3. After PANI is intercalated into MoO_3, the peak shape of the composite is similar but the area surrounded by has enlarged, which shows the intercalated PANI does not have much effect on

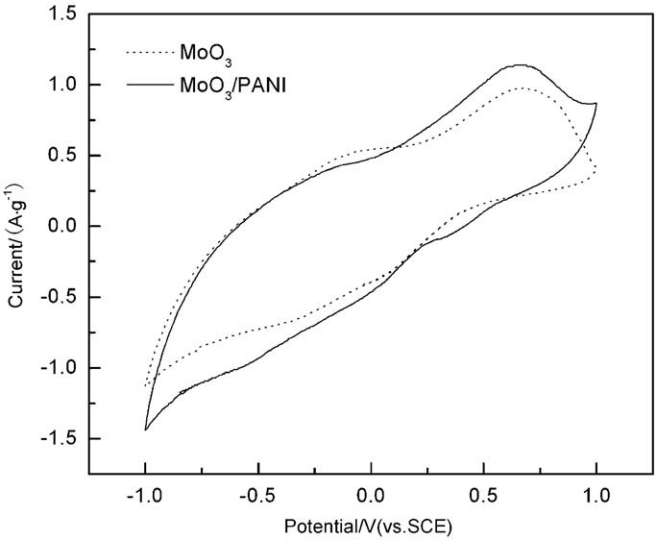

Fig. 5. Cyclic voltammograms of MoO_3/PANI and pure MoO_3 in 0.5 mol L^{-1} Li_2SO_4 electrolyte. The scan rate is 5 mV s^{-1}.

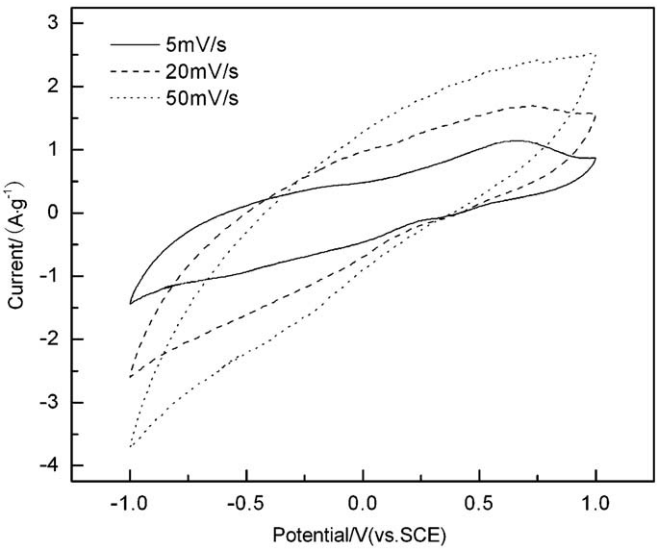

Fig. 6. Cyclic voltammograms at different scan rate of MoO_3/PANI electrode in 0.5 mol L^{-1} Li_2SO_4 electrolyte.

its redox features, but promotes Li^+ and/or electron transport. The reason may be that the interlayer spacing increased after PANI intercalated into the interlayer space; further, the intercalation and de-intercalation speed of Li^+ in the layered structure of the composite improved.

The whole charge and discharge process of carbon–MoO_3/PANI battery can be expressed as follows:

$$\text{carbon}-\text{cathode}: \ 6C + xLi^+ + xe^- \underset{\text{deintercalation}}{\overset{\text{intercalation}}{\longleftrightarrow}} Li_xC_6$$

$$MoO_3/\text{PANI}-\text{anode}: Li_x[\text{PANI}]_xMoO_3^{x-} \underset{\text{intercalation}}{\overset{\text{deintercalation}}{\longleftrightarrow}} [\text{PANI}^+]_xMoO_3^{x-} + xLi^+ + xe^-$$

$$\text{carbon}-MoO_3/\text{PANI}: \ 6C + Li_x[\text{PANI}]_xMoO_3^{x-} \underset{\text{discharge}}{\overset{\text{charge}}{\longleftrightarrow}} Li_xC_6 + [\text{PANI}^+]_xMoO_3^{x-}$$

Fig. 6 indicates the cyclic voltammetry curves at different scan rate of MoO_3/PANI electrode in Li_2SO_4 0.5 mol L^{-1} electrolyte with the cyclic scanning ranges from −1.0 to 1.0 V. According to Fig. 6, with the increasing of scan rate, the peaks of oxidation and reduction turn to be unnoticeable gradually, and the oxidation peak moves to the forward direction. All above phenomena indicate that it is a quasi-reversible oxidation–reduction reaction.

Fig. 7 shows the alternating current impedance of MoO_3/PANI electrode. The open circuit potential is −0.04 V, and the range of frequency is from 10^6 to 10^{-2} Hz. Fig. 7(b) is the partially enlarged drawing from the section of high frequency in Fig. 7(a). Two spectral lines of alternating current impedance both include a smaller semicircle (in the section of high frequency) and an oblique line with an angle of 45° (in the section of low frequency). It is believed that the semicircle in the section of high frequency is attributed to the charge transfer resistance and the capacitive reactance in the interface between the electrode and the electrolyte. The radius of the semicircles can indicate the magnitude of electrochemical reaction resistance. It is obvious that the semicircle radius of MoO_3/PANI composite is smaller than that of the pure MoO_3, suggesting that PANI improves the conductivity of the composite. The oblique line in the section of low frequency corresponds to the Warburg impedance by the diffusion of Li^+ in the solid phase of the electrode. In terms of the

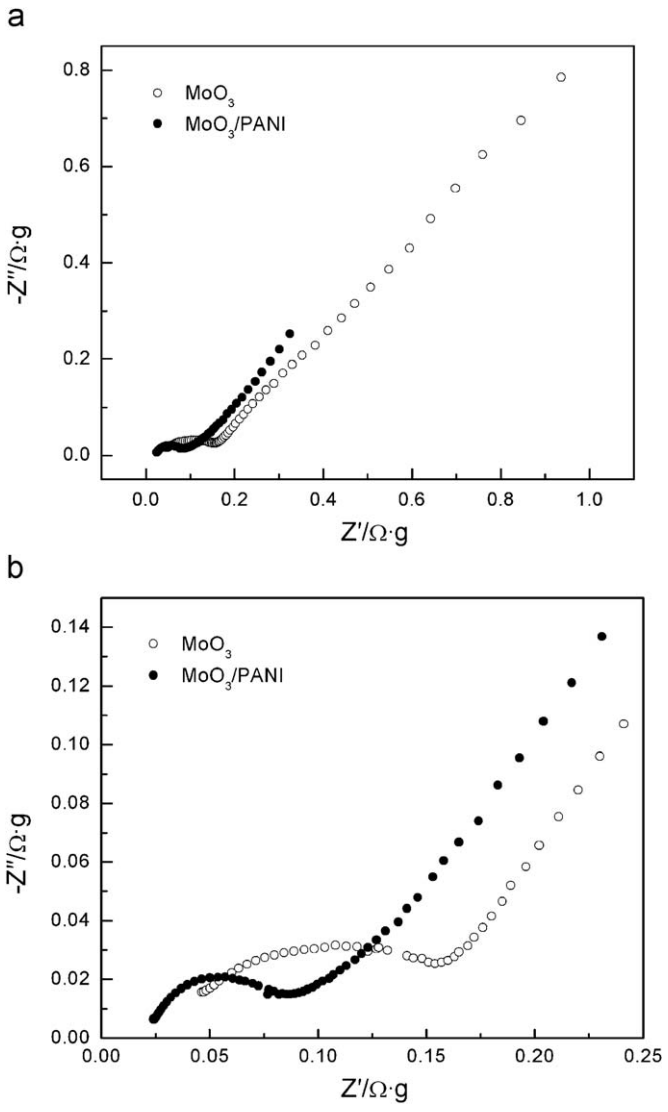

Fig. 7. (a) Alternating current impedance of MoO_3/PANI and pure MoO_3 electrode. (b) The partial enlarged drawing from the section of high frequency in (a).

value of capacitive reactance arc, the electrochemical reaction resistance of MoO_3/PANI electrode is lower than that of the pure MoO_3 electrode. What is more, according to Fig. 7(a), the ohmic resistance of MoO_3/PANI electrode is less than that of pure MoO_3 electrode, which indicates that the electrical conductivity of MoO_3 is increased by intercalating PANI into this composite.

With the increasing of the electrical conductivity of MoO_3/PANI composite, a reasonable explanation is that PANI exists as the form of electron conjugated extended chain, which is easy for the electron transfer. Besides high electron conductivity, polyamiline also can transfer proton and ions. Especially when MoO_3 has a large space structure, the main ions doping/dedoping from PANI will be Li^+, and further, improves the transfer of Li^+ into the MoO_3 layers and improves the conductivity of the MoO_3/PANI composite. In addition, former researches about this sort of material mainly focused on anhydrous solution system, while in this study we choose 0.5 mol L^{-1} Li_2SO_4 neutral aqueous solution electrolyte which is easy to prepare and use.

4. Conclusion

Our present study shows that alkylamine is used as the intercalation agent. After intercalating ANI monomer into the interlayer space of MoO_3 in advance, heat treatment at 120 °C for 3 d in air will cause the interlaminar ANI to polymerize, forming layered structure of MoO_3/PANI composite. We have discarded the traditional method which relies on the precursor of $(Li/Na)_xMoO_3$, initiator and aqueous solution system. Results of X-ray diffraction, SEM and differential thermal analysis indicate that when PANI is intercalated into the interlayer space of MoO_3, the distance between interlayers will be increased by 0.435 nm, but the composite itself still keeps a layered structure. The interlaminar ANI turns 90° during the polymerization process, existing in parallel with the interlayer plates of MoO_3. The results of electrochemical test demonstrate that the intercalation of PANI will not change its oxidation and reduction character, but it can promote Li^+ and/or electron to transmit. The electrode reaction of MoO_3/PANI composite is a quasi-reversible oxidation and reduction reaction. The alternating current impedance proves that if the resistance of MoO_3/PANI electrode reduces apparently, the electrochemical activity will increase correspondingly, the same as the relationship between the ohmic resistance and the electrical conductivity.

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