

PEDOT modified $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with enhanced electrochemical performance for lithium ion batteries

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Highlight

1. PEDOT modified $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was fabricated by a facile method.
2. Modified samples showed an improved rate performance.
3. PEDOT layer facilitated the electron transfer at the surface of electrode.

Abstract

Layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was modified by poly(3,4-dioxyethylenethiophene) PEDOT via a facile method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and infrared spectroscopy (IR). PEDOT modified samples exhibited both improved rate and cycle performance compared with the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. At a charge/discharge current of 1500 mA/g, the discharge capacity was improved from 44.3 to 73.9

mAh/g. The sample with 2 wt% and heat treated at 300 °C showed the optimized electrochemical performance. Galvanostatic intermittent titration technique (GITT) and cyclic voltammetry (CV) results indicated that the battery polarization of coated samples have been suppressed obviously because the PEDOT layer facilitated the electron transfer at the interface of electrode and electrolyte.

Keywords: $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, PEDOT, surface coating, rate, polarization

1. Introduction

Lithium ion battery has made great success in portable electronics since it was marketed by SONY. The ever increasing energy, power, cost and safety requirements of electric vehicles and stationary power impel the further promotions of lithium ion batteries. These performance improvements depend critically on innovations of electrode materials especially cathode materials [1]. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has been considered as a very promising cathode, in respect that it integrates the features of LiCoO_2 , LiNiO_2 and LiMnO_2 , and shows favorable benefits such as high capacity, thermal stability, low cost and safety [2]. Despite the fact that significant improvement for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ have been achieved, increasing of rate capability and cycle life still remain as necessary developments before it is more widely feasible application. The main reasons for the existed problems were ascribed to the battery polarization, low mass transfer and side-reactions at the interface of electrode and electrolyte during the charge/discharge cycles. It was found that the electrochemical behavior of electrodes is critically dependent on the surface chemistry [3]. Thus, effectively stabilization of the electrode surface by an appropriate coating layer can not only suppress the side-reactions occurred at the electrode/electrolyte interface, but also can improve the rate performance by facilitating the Li^+ and electron transfer between the electrode and the electrolyte [4]. Recent research result shows that coating of a surface layer on the cathode particles can stabilize the material structure and prevent the phase transformation upon cycling in some way, although

the exact mechanism of such stabilization effect by the surface coating is not very clear [5]. Therefore, it is of great important to develop of a suitable coating layer for a cathode material to promote its cycle and rate performance.

Previously reports demonstrated that conductive polymers, when used as a coating layer, showed positive effects on the performances $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Mn}_{0.13}\text{O}_2$ [6], LiFePO_4 [7] and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [8] etc. Poly-3,4-ethylenedioxythiophene (PEDOT), as a good electric conductor, has attracted the attention of battery researchers until recently. For example, Schougaard et al. fabricated poly(3,4-ethylenedioxythiophene) PEDOT/ LiFePO_4 composites by a soft chemical approach to enhance the rate capacity [9]. PEDOT/ LiCoO_2 composite has also been synthesized by electrochemical deposition [10]. *In situ* polymerization method was developed more recently by using Fe^{3+} as oxidant during preparation of PEDOT coated FeF_3 [11]. However, the effective coating of PEDOT on LiNiCoMnO_2 series cathode has not been investigated so far. For LiNiCoMnO_2 series cathode, the utilization of an external oxidant during in situ polymerization of the conductive coating layer would result in residue of the ion impurity in the final products. Thus, a facile and effective strategy to fabricate PEDOT modified LiNiCoMnO_2 series cathode should be developed toward superior rate and cycle performance.

Herein, we report the fabrication of PEDOT modified $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by a facile method. To avoid the introduction of foreign ions in the products, commercial PEDOT was used as coating material. Evidence of the surface coating was obtained by TEM and IR. Rate and cycle performance were conducted to investigate the PEDOT effects on the electrochemical performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. CV on cycled cells were performed to demonstrate the improvements of electrochemical properties after PEDOT modification.

2. Experiment

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was prepared according to the reference [12]. 0.5g of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and target amount of PEDOT aqueous solution were mixed and

grounded in an agate mortar for more than 30 min, then the mixture were dried at 80 °C in vacuum for one night. The final product was obtained by annealing at different temperature in air. To explore the optimum coating condition, the coating amount was changed from 1 wt% to 4 wt% and the annealing temperature varied from 200 °C to 400 °C. For convenience, the samples were marked as X wt%-T in which X represents the coating amount and T represents the annealing temperature.

XRD (Bruker D8 with Cu $K\alpha$ radiation, $\lambda= 0.1546\text{nm}$) was used to characterize the structure of the pristine and coated samples. The coating layer and surface morphology before and after modification were examined by TEM on a JEOL 3100F instrument. The PEDOT layer was examined by Fourier transform infrared (FTIR) measurements on a JASCO instrument of FT/IR-6200 from 4000 to 400 cm^{-1} . Raman spectroscopy was conducted on a Micro Raman spectrophotometer (Ventuno21, JASCO).

Electrochemical performance of all the samples were conducted using coin-type cells (CR2032) consisting of a cathode, a Celgard separator and a Li metal with 1 M LiPF_6 in EC/DEC (1:1 vol%) as the electrolyte. All the cells were assembled in an Ar-filled glove box. The cathode electrode was fabricated from a mixture of active material : acetylene black : polytetra-fluoroethylene (PTFE) 80:15:5 (mass%) impressed on an aluminum mesh current collector. The galvanostatic charge-discharge tests were conducted on a Hokuto Denko in a potential range of 2.8-4.5V (vs. Li/Li^+) at a certain current density. CV was examined by coin cells on a Solartron Instrument Model 1287 with different scan rates. Thermal stability was examined by differential scanning calorimetry (DSC) on EXSTAR 7000 X-DSC in a temperature range of 30-320 °C at a heating rate of 10 °C/min. Before DSC measurements, the cells were first charging to 4.3 V at a current of 15 mA/g and then charge at 4.3 V for another 3 hours. After that, the cells were disassembled in an Ar filled glove box, the charged samples were collected and sealed in Al-pan for DSC measurements.

3. Results and discussion

XRD patterns of the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and 2 wt%-300 PEDOT coated samples are showed in Fig.1. All the patterns of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, can be well indexed to the space group $R-3m$. The splitting of the peaks (108), (110) and (006), (102) is an indication of a well ordered $\alpha\text{-NaFeO}_2$ structure, the ratios of I_{003}/I_{104} is above 1.2, which indicates the desirable cation mixing [13,14]. For the coated sample, all the diffraction peaks can also be well accordance with the pristine sample, showing negligible structure changes by surface coating. No impurities or secondary phase were observed from XRD patterns. The lower and thinner organic coating layer can not be detected by XRD. In addition, the relatively low heat treatment temperature seemed not allow for the formation of new phase or structure.

SEM images of pristine and 2 wt%-300 coated samples in Fig. 2 show the surface morphology and particle size changes after surface modification. Both of the samples exhibit secondary spherical structures with a diameter varied from 1 μm to 5 μm . The primary particle size is in the range of 200-400 nm. There are no obvious changes in particle size after surface coating. The edge and surface is clean and smooth for the pristine as shown in Fig. 2c. In contrast, it becomes rough and ambiguous after coating as shown in Fig. 2d. In order to observe the detailed existence of PEDOT on the surface, TEM were conducted on different samples. Fig. 3a displays the image of as prepared pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with a clear and clean surface. For 4 wt% PEDOT coated sample, a coarser surface with a coating layer about 10 nm can be seen clearly in Fig.3b, while only a 4 nm coating layer can be observed for the 2 wt% coated sample as shown in Fig. 3c. With the decreasing of coating amount, the surface layer became thinner. Heat treatment can decompose part of the organic component. Thus, after annealing the 2 wt% PEDOT coated sample at 300 $^\circ\text{C}$ for 5 h, a thinner layer can be obtained as observed in Fig. 3d, there is only a very thin amorphous layer on the particle surface. From these results, we can find that a heat treating even at 300 $^\circ\text{C}$ can decompose part of the amorphous coating layer.

The existence of PEDOT on the particle surface can be further confirmed by comparison of the IR spectrum of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and coated sample. As shown in Fig. 4, pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ exhibits two well separated band at 590

and 540 cm^{-1} which come from the M-O vibration [15]. No significant blue-shift or red-shift can be observed after surface coating in this region, indicating no strong interaction between PEDOT and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, or no distortion of the intrinsic lattice structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The presence of PEDOT is confirmed by the C=C ring and C-O-R vibration at about 1180 cm^{-1} and the C-S vibration at 939 cm^{-1} [9]. These results demonstrate that the PEDOT has coated on the surface. Raman spectra were also employed to obtain more information about the surface structure as shown in Fig. S1. Raman bands centered at about 590 cm^{-1} can be assigned to the M-O symmetrical stretching vibration which attribute Raman modes of A_{1g} of the layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [16-18]. No Raman bands from PEDOT is recorded due to the low weight content of the coating layer. Raman bands of the heat treated samples exhibit a 4 cm^{-1} blue shift compared to the samples without heat treatment. The reason might be that the heat treatment leads to more closely interact between the surface coating layer and the core material so that the M-O vibration at the surface layer was influenced. It is also evidenced the heat treatment made the coating layer contact with the core $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ more closely.

Coin cells using metallic Li as the counter electrode were assembled and galvanostatic charge/discharge test is employed to evaluate the cycle and rate performances after surface modification by PEDOT. The charge-discharge cycle performance was conducted in the voltage range of 2.8-4.5 V at a current of 150 mA/g. As shown in Fig. 5a, the pristine material suffered a serious capacity fading upon cycling with a discharge capacity of 116.6 mAh/g at the 80th cycle. While for the PEDOT coated samples, the discharge capacities of 1 wt%-300, 2 wt%-300 and 4 wt%-300 are 125.6, 133.7 and 132.2 mAh/g at the 80th cycle, respectively. This result clearly demonstrated that the PEDOT coating layer can improve the cycle performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and also make us believe that an appropriate thickness of coating layer is very important to the coating effects.

Rate capability of cathode is an important feature for the cathode in widely application especially as power source for automobile. Actually, this work is originally inspired with the expectation that the conductive polymer can improve the

surface conductivity to enhance the rate capacity. Thus, the rate capacities were examined as shown in Fig.5b. In order to get the optimum coating condition, the influence of heat treatment temperature was studied on 2 wt% PEDOT coated samples have been studied. All the rate tests were conducted in the potential range of 2.8-4.5V (vs. Li^+/Li) with varied current densities from 75 mA/g to 1500 mA/g. The rate performance of 2 wt% coated samples without any heat treatment is only slightly improved in comparison with the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. After annealing, there is an obvious improvement of the discharge capacity especially at high current densities. For example, at the same charge-discharge current of 1500 mA/g, the coated samples with no heat treatment, 200°C heat treatment, 300°C heat treatment, 400°C heat treatment delivered a discharge capacity of 44.3, 73.8, 73.9, and 59.2 mAh/g, respectively. In contrast, the pristine sample only showed a discharge capacity of 41.8 mAh/g at the charge-discharge current of 1500 mA/g. It is obviously the different heating temperature played an important role on the PEDOT coating effects. This may be because the heat treatment not only results in some changes of the surface morphology as has been confirmed by TEM, but also an effect on the vibrational of M-O at the interface of coating layer and the core material as evidenced by Raman spectrum. The two changes together promote the electron and ion transfer between the electrode and electrolyte. Thus, the enhancement of electrochemical performance by surface coating can be interpreted from two aspects. One is the coating layer with heat treatment obviously alleviate the surface polarization by facilitating the electron transfer at the interface of electrode and electrolyte. The other is the coating layer separates the active material from directly contraction with the electrolyte, which can impeded the side-reactions at the interface. It is understandable that the charged electrodes with their metal ions at high valence states are easy to react with the electrolyte and lead to the capacity fading.

In order to better understand the effects of the improvement of electrochemical performance, the galvanostatic intermittent titration technique (GITT) measurements on fresh and cycled cells were conducted to investigate the polarization effects before and after cycled charge/discharge processes. Before the GITT measurements, the cells

were firstly galvanostatic charge/discharged for a certain number of cycles. GITT measurements were performed by charging/discharging the aged cells at a constant current (20 mA/g) for an interval of 1 hour followed by an open circuit stand for 3 hours to allow the cell voltage to relax to its quasi-equilibrium state. As shown in Fig. 6a and 6b, there are no obvious differences between the pristine and the coated sample for the fresh cells. However, after 100 charge/discharge cycles, the differences in charge potential for the pristine and coated sample became more obviously. The increase of charge potentials upon cycling is mainly caused by the aggravation of surface polarization. There is an obviously increase of charge potentials for both of the pristine and coated samples. If define the difference of charge potentials between the fresh cells and cycled cells as ΔE , it is clear that ΔE for the pristine is larger than that of the coated sample. The PEDOT coating layer suppresses the deterioration of the surface polarization at a certain degree. It is a general consensus that mass transport in the electrolyte and the solid phase of the electrodes, contact problems between the solid phases and slow electrochemical reactions account for the polarization of the batteries [19]. That is to say, the PEDOT coating layer suppressed the surface polarization by facilitating the mass transfer at the interface of electrode and electrolyte. As the increasing of charge/discharge current, there is an increasing of charge potential and a decreasing of discharge potential which implies a decreasing energy efficiency. This should be mainly attributed to the polarization of the batteries. The average charge potential of pristine sample was 4.32 V when the charge-discharge current at 1500 mA/g, while, the corresponding value for the 2 wt%-300 PEDOT coated sample was 4.21 V. Apparently, the PEDOT coating layer suppressed the increase of charge potential especially at a high charge-discharge current. Since the polarization effects depends on the C-rate, the average charge/discharge potentials with different charge discharge currents is shown in Fig. 6d. The average charge (discharge) potentials increase (decrease) obviously with the increasing of C-rates. The PEDOT coated sample showed a suppressed effects on the changes of average potentials along with the changes of C-rate. This is primarily because the PEDOT coating layer prevent the surface polarization by promoting the

mass transfer at the interface of electrode and electrolyte. The surface coating by PEDOT not only improve the charge/discharge capacities, but also enhance the energy efficiency.

Cyclic voltammetry (CV) is a useful tool to study the electrochemical performances and electrode kinetics of oxide materials. CV at different scan rates was performed to evaluate the PEDOT coating effects. CV measurements were conducted at the voltage range of 2.0-4.6V (vs. Li^+/Li) with varied scan rates from 0.1 to 0.5 mV/s on both of the fresh and cycled cells of pristine and 2 wt%-300 PEDOT coated samples. As shown in Fig.7, at a sweep rate of 0.1 mV/s, a couple of well refined peaks at 3.98/3.70 V for the pristine sample and 3.94/3.69 V for the coated samples were recorded. These peaks originated from the redox of $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple [20]. After charge/discharge cycles, as shown in Fig. 7c and 7d, there is an obvious shift of both of the cathodic and anodic peaks. The cathodic peaks shifted to a higher potential while the anodic peaks shifted to a lower potential. After the charge/discharge cycles, the surface polarization become more seriously due to the side-reactions between the electrode and electrolyte. At high sweep rates, there are also some changes should be noted. Firstly, the current density and redox peaks area increase for all of the four samples, since the peak area divided by the sweep rate which present the capacity. Secondly, there are a increase cathodic peak potentials which may result from the polarization of the batteries. In contrast, there were almost no changes for the anodic peak potentials of all the samples. The un asymmetric changes of the charge and discharge processes make us aware of that the polarization of batteries showed a greater impact on the charge processes than the discharge processes. For the comparison of the changes of cathodic peak potentials, plots of cathodic peak potentials versus sweep rates were shown in Fig. 8. The peak potentials of the pristine samples is remarkably larger than the coated samples, especially at higher sweep rates. The potential difference means that polarization effects become more manifest at higher sweep rate. The battery polarization is mainly caused by the mass transfer barriers at the interface of electrode and electrolyte. The shift level of the coated samples decreases compared with the pristine one on both of the fresh and cycled

cells, which demonstrates the alleviation of polarization due to the promotion of mass transfer properties with the help of PEDOT coating layer.

Thermal stability of cathode materials plays an important role in judging their practical application in lithium ion batteries. A DSC study was conducted after charging the cathodes to 4.3 V to evaluate the effects of PEDOT coating on the thermal stability of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Fig. 9 shows the DSC profiles of the pristine and 2 wt%-300 PEDOT coated samples. The pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ showed an exothermic peak at 283.1 °C with an exothermic heat generation of 129.0 J/g. While the exothermic peak of coated samples shifted to 284.6 °C with an exothermic heat generation of 69.3 J/g. The thermal decomposition temperature showed a minor increase, but the exothermic heat generation decrease obviously. The improved thermal stability of the coated sample rooted in the PEDOT coating layer, which prevents the oxidized cathode electrode from directly contact with the electrolyte, thus, reducing the exothermic reaction.

4. Conclusion

The effect of PEDOT coating on electrochemical performances of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode was investigated and the optimum coating condition is with coating amount of 2 wt% and heat treated at 300 °C. The rate capacity have been significant improved from 41.8 mA/g to 73.9 mAh/g at a charge-discharge current of 1500 mA/g. The energy efficiency has also been improved obviously. Compared the GITT curves and varied sweep rate of CV before and after charge-discharge cycles, the PEDOT coating layer obviously suppressed the battery polarization, especially at a high charge/discharge current. The PEDOT coating layer was found to improve the thermal stability and prevent the electrode from direct interaction with the electrolyte. The main reason for the improved performance of PEDOT-coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ could be attributed to the conductive polymer layer promote the mass transfer at the interface of electrode and electrolyte which alleviate the surface polarization. This study demonstrated that surface coating with PEDOT is a facile but

effective way to enhance the rate capabilities of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for lithium ion battery.

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Figure Caption

Fig. 1 XRD patterns of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Black line) and 2 wt% PEDOT-300 (Red line);

Fig.2 SEM images of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (a, c) and 2 wt% PEDOT-300 °C (b, d);

Fig.3 TEM images of (a) pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder, (b) 4 wt% PEDOT-300 °C, (c) 2 wt% PEDOT without heat treated (d) 2 wt% PEDOT-300 °C;

Fig.4 FTIR of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Black) and PEDOT-coated sample (Red);

Fig.5 (a) Cycle performance of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and PEDOT coated samples with different coating amount in the voltage range of 4.5 and 2.8 V vs. Li^+/Li ; (b) rate performance of pristine and 2 wt% PEDOT coated samples with different annealed temperature

Fig.6 GITT of pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (a) and 2 wt% PEDOT-300 coated sample (b) on fresh (black line) and cycled cells (red line); charge-discharge profiles at 1500 mA/g (c) and average potential with different charge-discharge current (d);

Fig.7 CV curves of pristine and 2 wt% PEDOT-coate-300 °C sample before and after charge-discharge cycles at a series of sweep rates. (a) pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ before cycles; (b) 2 wt% PEDOT-coate-300 °C sample before cycles; (c) pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ after charge-discharge cycles; (d) 2 wt% PEDOT-coate-300 °C sample after charge-discharge cycles;

Fig.8 Changes of peak potentials as function of scan rate (a) on fresh cells; (b) on charge-discharged cells;

Fig.9 DSC profiles of pristine and 2 wt% PEDOT-300 electrodes charged to 4.3V.

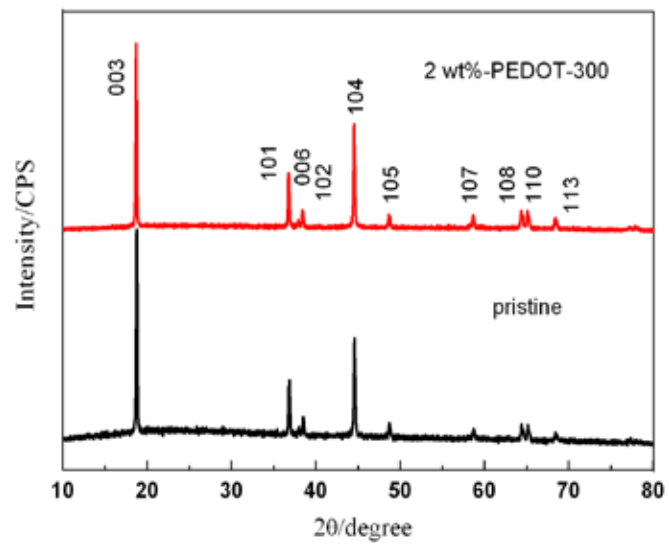


Figure 1

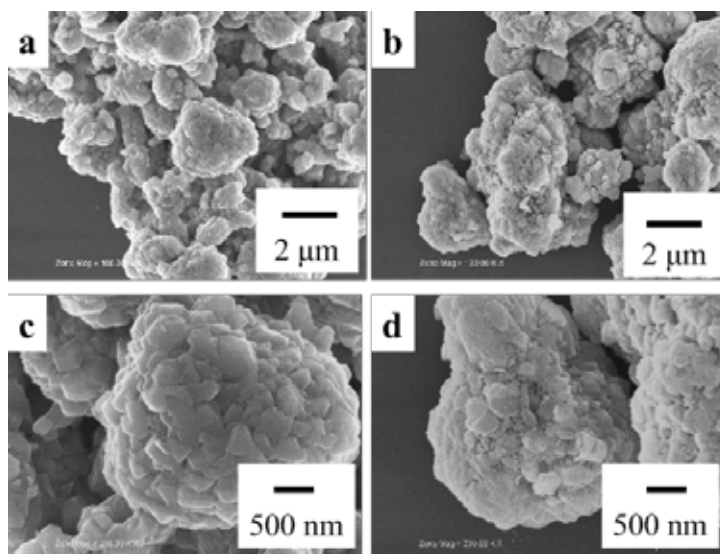


Figure 2

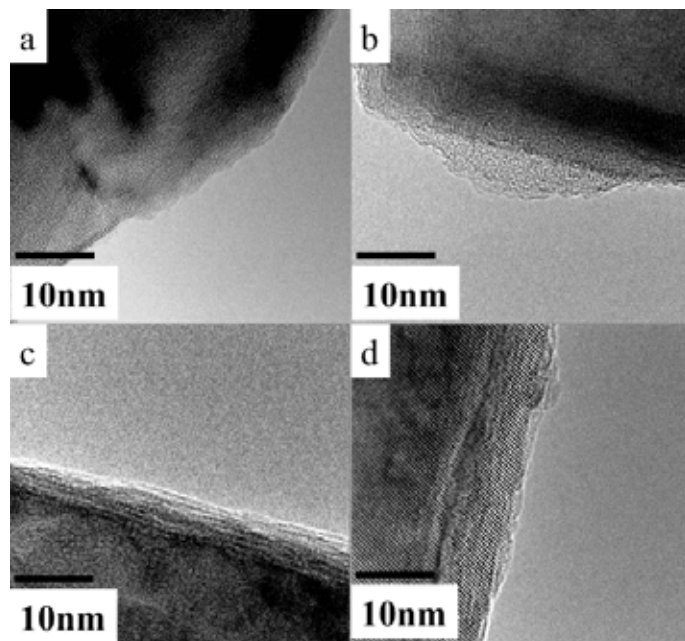


Figure 3

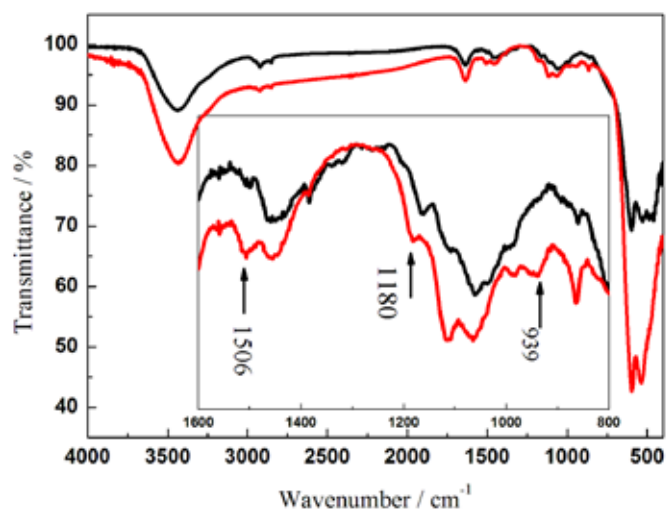


Figure 4

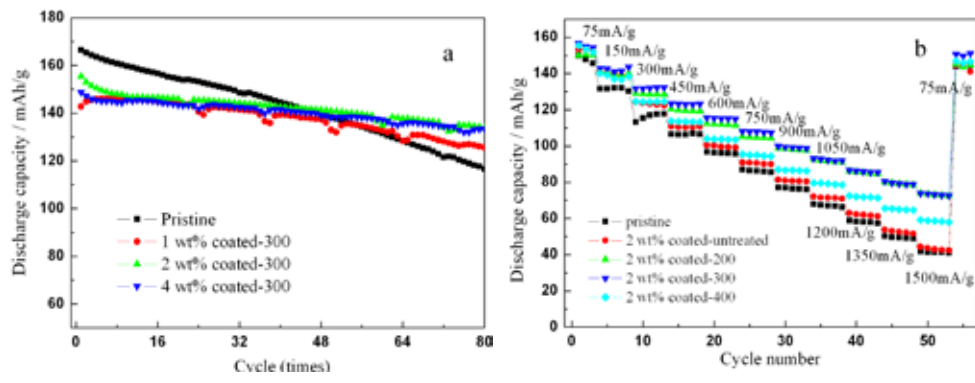


Figure 5

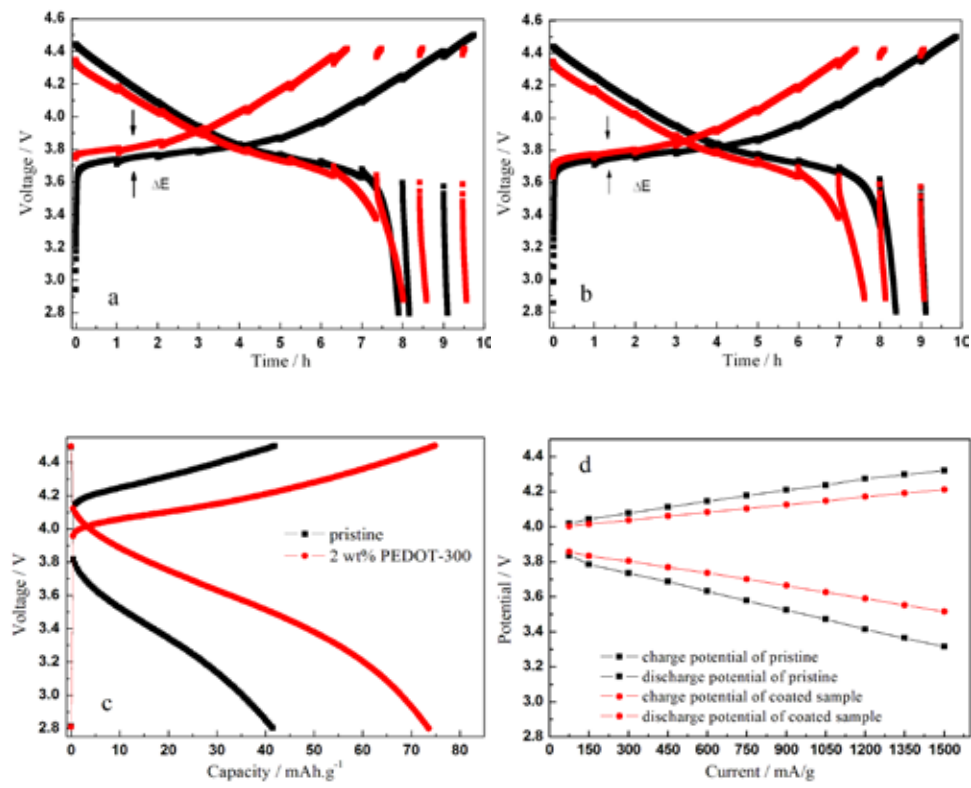


Figure 6

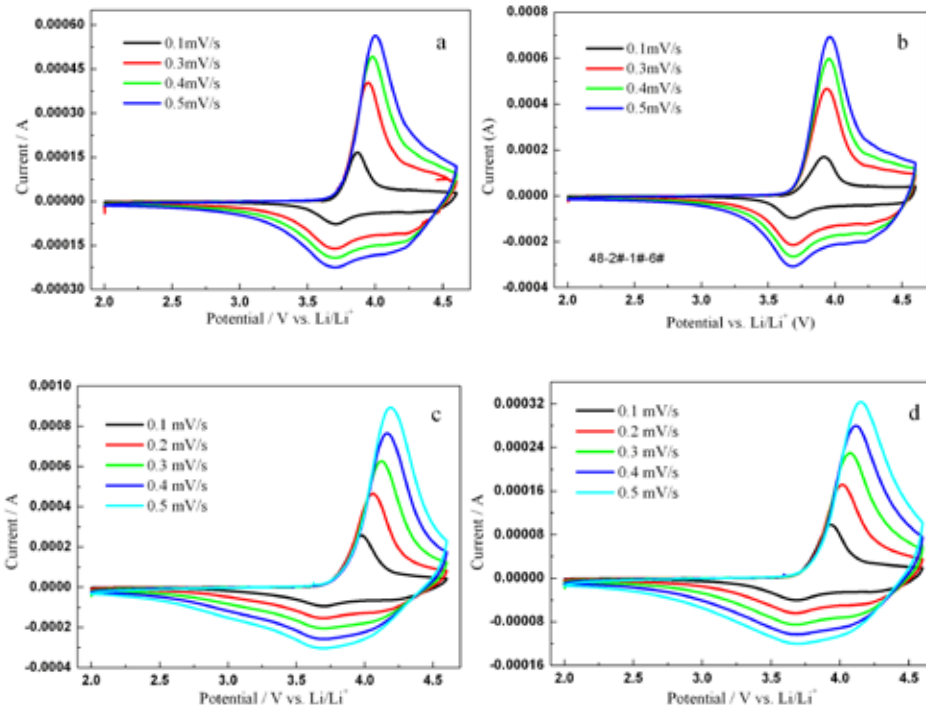


Figure 7

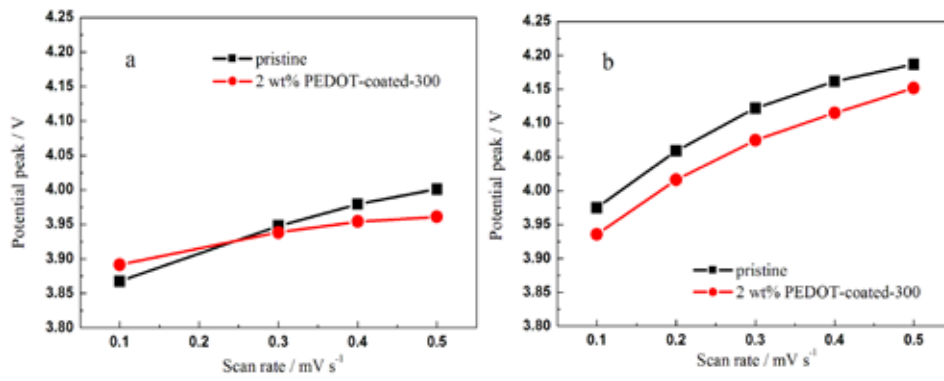


Figure 8

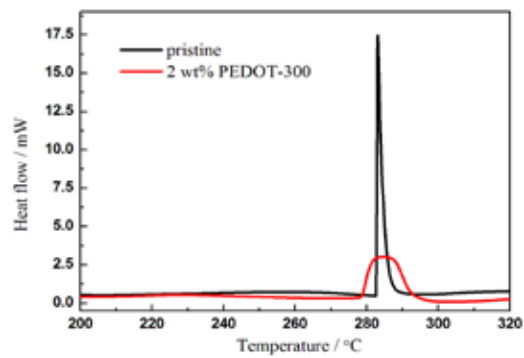


Figure 9

Supporting Information

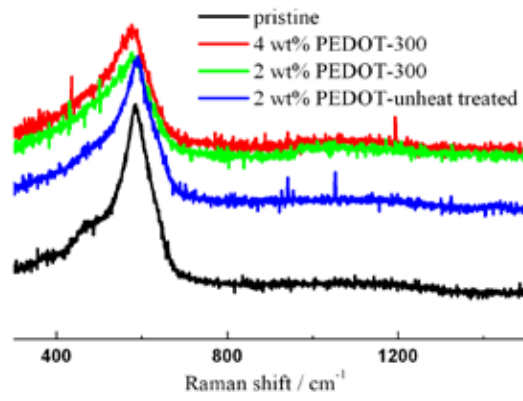


Fig. S1 Raman spectrum of pristine and PEDOT coated samples