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ORIGINAL PAPER

# An aqueous rechargeable lithium battery based on doping and intercalation mechanisms

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**Abstract** An aqueous rechargeable lithium battery (ARLB) using an electroactive polymer, polypyrrole (PPy), as a negative electrode; a lithium ion intercalation compound $LiCoO_2$ as a positive electrode; and $Li_2SO_4$ aqueous solution as an electrolyte and its working mechanism are described. The charge/discharge process is associated with the doping/un-doping of anions at the negative electrode and intercalation/deintercalation of lithium ions at the positive electrode. The average output voltage of the PPy//$LiCoO_2$ battery is about 0.85 V. This battery exhibits excellent cycling performance. This new technology solves the major problem of poor cycling life of ARLBs and will provide a new strategy to explore advanced energy storage and conversion systems.

**Keywords** Aqueous rechargeable lithium battery (ARLB) · $LiCoO_2$ · Electroactive polymer · Doping/un-doping

## Introduction

Electrochemical energy conversion and storage systems are playing an important role in the progress of humankind and in almost all aspects of daily life, including accommodation, transportation, military, and space exploration [1]. Common and well-known batteries, such as Zn//$MnO_2$, Zn//AgO, lead acid, Ni–Cd, Ni–MH, and lithium ion batteries, were and are widely used. However, the progress of technology raises more and more tasks for batteries, such as power leveling and electricity storage [1, 2]. As a result, exploring new electrochemical power sources is of great importance to improve the utilization of natural resources and reduce the emission of $CO_2$ to promote a sustainable development for humankind.

Since the invention of the lithium ion battery, which is based on intercalation phenomena and is different from the former types of batteries, which were only based on redox processes, in the early 1990s [3, 4], the progress of new battery systems has been very limited. In 1994, rechargeable lithium batteries based on intercalation processes using aqueous electrolytes were introduced [5, 6], and recently, their performance was greatly improved due to the use of new anode materials such as $LiV_3O_8$ [7-9]. However, the capacity of the above systems still fades [7, 8].

Here, we report on an aqueous rechargeable lithium battery (ARLB) based on doping and intercalation mechanisms, whose average output voltage is about 0.85 V. It presents excellent cycling performance in an aqueous $Li_2SO_4$ electrolyte solution, which is evidently very safe for large-scale energy storage.

## Experimental

Crystalline $LiCoO_2$ was prepared by a conventional solid-state reaction by reacting stoichiometric amounts of $Li_2CO_3$ with $Co_3O_4$ at 800°C for 24 h followed by cooling to ambient temperature, resulting in a black solid [7]. The resulting product was ground into powder and

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characterized by X-ray diffraction. The structure of $LiCoO_2$ is rhombohedral (R3m space group) with lattice parameters $a$ = 2.816 Å and $c$ = 14.051 Å in a hexagonal setting. Polypyrrole (PPy) was prepared by chemical oxidative polymerization of the corresponding monomer (pyrrole) in an aqueous medium as described elsewhere [10]. Pyrrole (2 ml) was added into a flask with 150 ml of distilled water under magnetic stirring. The oxidant $(NH_4)_2S_2O_8$ was dissolved in 50 ml of water and then added dropwise into the flask after removal of dioxygen in the water by purging with nitrogen. The reaction was carried out for 8 h at 0°C. The precipitated PPy was filtered off and washed with distilled water. The PPy powder was dried in vacuum at 60°C for 8 h.

Scanning electronic microscopy (SEM), X-ray diffraction (XRD), and Fourier transformation infrared spectroscopy (FT-IR) were performed with a Philips XL 300 microscope, a D8 Bruker powder X-ray diffractometer, and Nicolet-360 IR spectrometer, respectively.

Galvanostatic discharge and charge testing was performed with a cycler LAND Electronic controlled by a personal computer at a constant current density. The preparation of the negative and positive electrodes was conducted in the same way. The electrode was prepared by pressing a powdered mixture of the sample, acetylene black, and poly(tetrafluoroethylene), in a weight ratio of 80:10:10, and nickel mesh as a current collector into pellets about 1 $cm^2$ in area and 300 μm in thickness. A three-electrode electrochemical cell was employed for cyclic voltammetric (CV) measurement in 10 ml saturated $Li_2SO_4$ solution (pH = 7). A saturated calomel electrode (SCE) and Ni-mesh were used as the reference and the counter electrodes, respectively.

## Results and discussion

Figure 1 shows the SEM micrograph, XRD pattern, and FT-IR spectrum of the prepared PPy particles. The diameter of the prepared PPy particles is about 200–400 nm. At $2\theta = 11.5^{o}$ and $26^{o}$, there are two broad peaks in its XRD pattern, indicating the existence of a short range order and an ordered structure between the PPy chains [11]. In Fig. 1c, characteristic bands of PPy can be observed at 1,549 $cm^{-1}$ (C = C stretching vibration of doped PPy ring), 1,468 $cm^{-1}$ (C–N stretching mode of the doped PPy), 1,380 $cm^{-1}$ (C–H or C–N in-plane deformation modes), 2,300–2,400 $cm^{-1}$ (overtones and combinations of $CH_2$ and $NH_2$ stretching and wagging vibrations), and around 3,500 $cm^{-1}$ (N–H and C–H stretching vibrations) [12]. In addition, characteristic bands of $SO_4^{2-}$ anion can be identified at 981, 597, and 486 $cm^{-1}$, corresponding to its $\nu_1$(A1), $\nu_4$(F2), and $\nu_2$(E) modes, respectively [13]. The existence of $SO_4^{2-}$ indicates that PPy chains were partially doped by the $SO_4^{2-}$ anions during the oxidation reaction [12, 14].

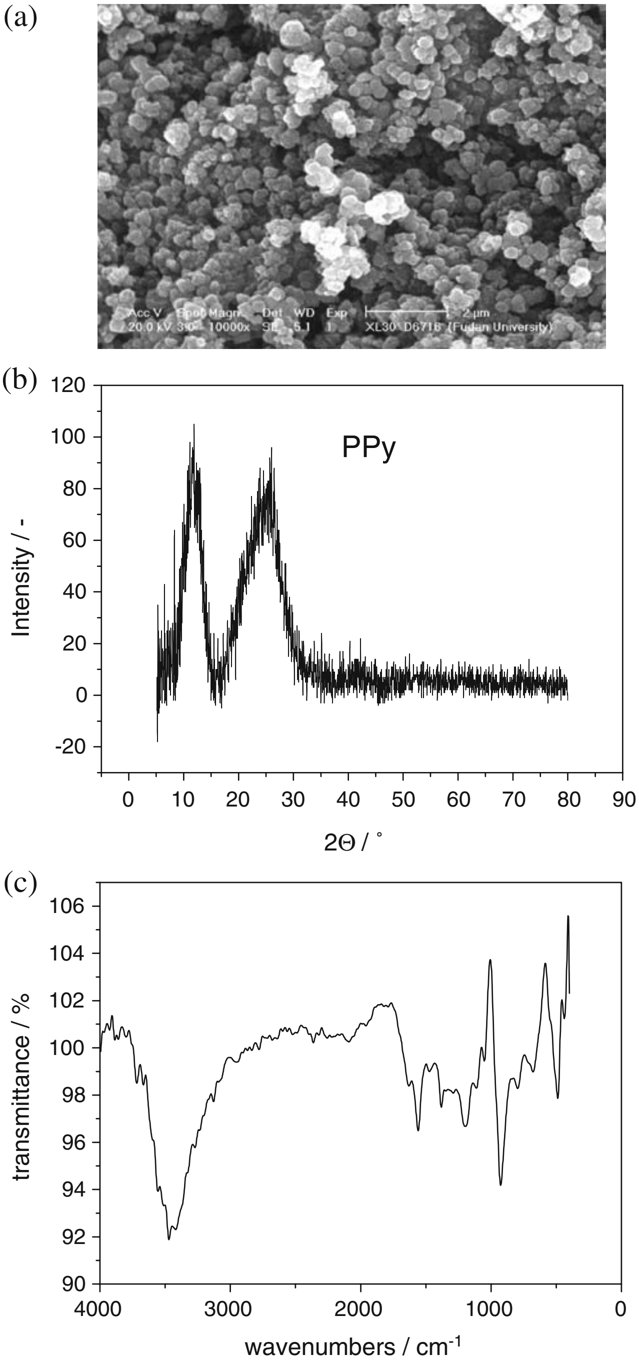

**Fig. 1** SEM micrograph (**a**), XRD pattern (**b**), and FT-IR spectrum (**c**) of the as-prepared PPy powder

The CV (starting point is at 0.0 V) of the PPy electrode in the saturated $Li_2SO_4$ solution is shown in the left curve of Fig. 2a. One pair of redox peaks situated at $E_{SCE} = -0.46$ V and $-0.15$ V were observed, respectively. The evolution of hydrogen in the aqueous electrolyte occurs

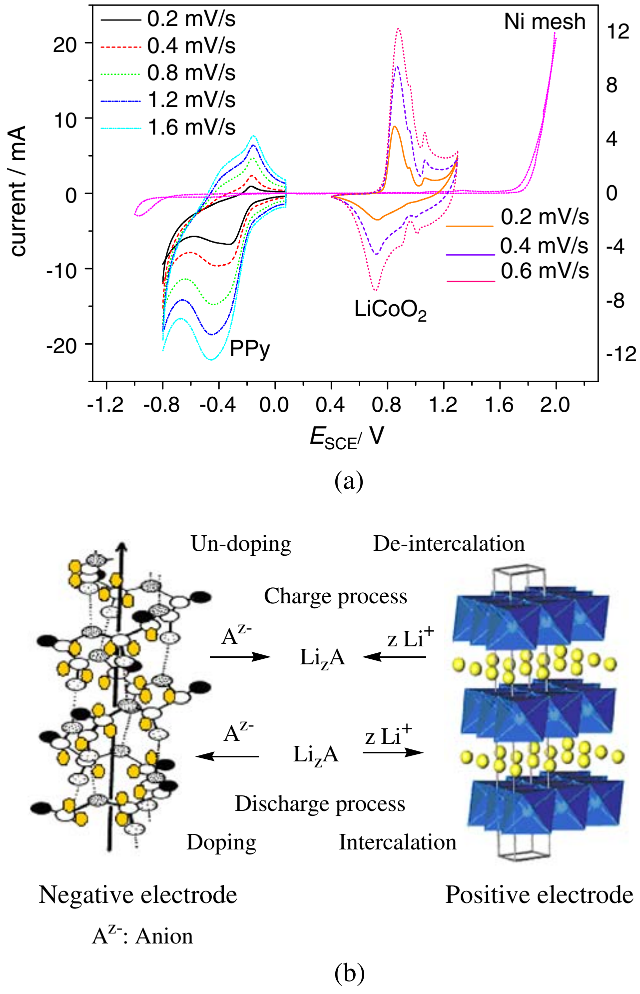

**Fig. 2** **a** CVs of PPy, $LiCoO_2$, and nickel mesh in saturated $Li_2SO_4$ solution and **b** principle of the ARLB system based on doping/un-doping (negative) and deintercalation/intercalation (positive) electrodes

at much lower potential, about $E_{SCE} = -1.0$ V, suggesting that PPy is very stable during the doping and un-doping processes. It is well known that some electroconductive polymers, such as PPy, can be used as positive electrode involving doping/un-doping of anions (*p*-type doping) [14, 15]. In fact, PPy can also be reduced and doped with cations (named *n*-type doping). However, the potential of *n*-type doping in organic electrolyte is much lower than that of $Li^+/Li$. Consequently, in the aqueous solution, only *p*-type doping and dedoping can take place, which is expressed as follows:

$$(\mathrm{Py})_n + ny\,\mathrm{A}^- \underset{\text{dedoping}}{\overset{\text{doping}}{\rightleftharpoons}} (\mathrm{Py}^{y+}\,y\mathrm{A}^-)_n + ny\,e^- \tag{1}$$

where Py is the monomer repeat unit of the electroactive polymer and $A^-$ is the electrolyte anion. The left curves in Fig. 2a show this doping and dedoping processes. According to the FT-IR spectrum, pristine PPy was initially doped with anions. Consequently, the current peaks are not due to the doping and dedoping with $Li^+$ ions [9]. Evidence regarding the identity of the doping anion is limited. However, since the current peaks associated with doping and dedoping with $HSO_4^-$ will be situated at higher electrode potentials, in the present case, they are most likely caused by doping and dedoping with $SO_4^{2-}$.

Positive electrode materials for lithium ion batteries such as $LiCoO_2$, prepared by solid-state reaction, are well known as good materials for reversible lithium intercalation in organic electrolytes [1, 16, 17]. It offers a good reversible intercalation and deintercalation of lithium ions in the aqueous electrolyte (see right curves in Fig. 2a, starting point is at 0.4 V), and the evolution of oxygen does not happen until about $E_{SCE} = 1.7$ V due to its overpotential [7, 18], suggesting good stability of $LiCoO_2$. It is worthwhile to note that a stable counter electrode such as $Li_{0.5}Mn_2O_4$ presents excellent cycling behavior [19], which indicates that the capacity fading of previous ARLBs is not mainly related to the positive electrode but to the negative electrode.

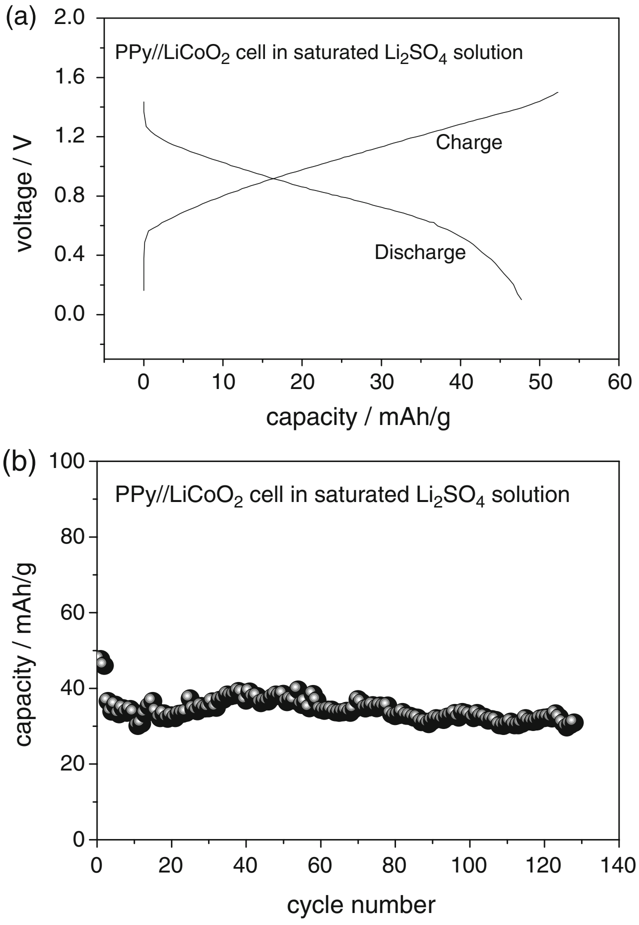

**Fig. 3** **a** Charge and discharge curves in the first cycle and **b** cycling behavior of the ARLB based on doping (PPy) and intercalation ($LiCoO_2$) compounds at 0.1C rate

Based on the results from Fig. 2a, it can be understood that an ARLB can be built using the dopable polymer as the negative electrode and the lithium intercalation compound as the positive electrode. During the charging process, lithium ions deintercalate from the positive electrode ($LiCoO_2$) into the aqueous solution and anions of $SO_4^{2-}$ dedope from the negative electrode (PPy) into the aqueous solution. The $Li^+$ ions and $SO_4^{2-}$ anions combine together into neutral $Li_2SO_4$. During the discharging process, lithium ions in the aqueous solution intercalate into the positive electrode and $SO_4^{2-}$ anions move into the negative electrode. This principle is schematically illustrated in Fig. 2b. The electrochemical processes of the positive electrode are similar to those of lithium ion batteries and previous concepts of earlier ARLBs [5, 7, 8]. The electrochemical process of the negative electrode is somewhat similar to that of the positive electrode for a battery using lithium metal as the negative electrode and conductive polymers as the positive electrode [14]. Since the reaction (positive for the latter case) of PPy is reversible, the electrochemical process is also reversible. It is obvious that this is the first rechargeable battery system to combine the above two processes into one battery system, this is also different from that using graphite as negative and PPy as positive electrodes [20].

The charge and discharge curves in the first cycle and the cycling behavior of the PPy//$LiCoO_2$ cell are shown in Fig. 3. In the first cycle, the charge and discharge capacities are 52.2 and 47.7 mAh/g based on the weight of the electrodes, and the coulombic efficiency is 91.4%. The average charge and discharge voltages are 1.0 and 0.85 V, respectively. Apparently, there is no evident capacity fading during the first 120 cycles, except for the first two cycles, this is completely superior to the present rechargeable lithium batteries. This can be ascribed to the good stability of the two electrodes during cycling in the aqueous electrolyte: (1) PPy is well known to be an excellent material for supercapacitors because of its highly reversible doping and dedoping; cycle numbers can be above 1,000,000 [21] and are superior to vanadium-based oxide negative electrodes such as $VO_2$ and $LiV_3O_8$ [5, 7, 22, 23]; and (2) $LiCoO_2$ has a very good cycling behavior in aqueous electrolytes [19].

The capacity density of this ARLB system is higher than that of lead acid rechargeable batteries, and smaller than that of Ni–MH and lithium ion batteries. It is known that the reversible capacity of $LiCoO_2$ can be up to 140 mAh/g in organic electrolytes and that of PPy about 120 mAh/g [1, 14]. If the capacities of the electrodes are increased to that level in organic electrolytes and $LiMn_2O_4$ is used to replace $LiCoO_2$, this system will have great promise since this kind of battery is very safe for large-scale energy storage and conversion and the rate capability will be very good [18, 19]. In addition, its assembling process is very easy and does not require strict control of the humidity of the environment. Furthermore, the price for each cycle will be quite competitive, due to the excellent cycling behavior. Of course, further exploration of new anode materials with lower potentials and higher capacities will be of great interest to get higher output voltages.

## Conclusions

An ARLB based on doping and intercalation mechanisms was successfully built up. It uses PPy as the negative electrode, $LiCoO_2$ as the positive electrode, and an aqueous solution of $Li_2SO_4$ as the electrolyte. The principle for this system is based on doping/dedoping and intercalation/deintercalation, and is different from the working mechanisms of previous battery systems. During the charging process, lithium ions deintercalate from the positive electrode into the solution and anions dedope from the negative electrode into the solution. During the discharging process, anions dope into the negative electrode and lithium ions intercalate into the positive electrode. The electrode materials of the cell are very stable during the charge and discharge processes, and excellent cycling behavior and satisfactory capacity density have been obtained.

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