Developing Polymer Cathode Material for the Chloride Ion Battery

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ABSTRACT: The chloride ion battery is an attractive rechargeable battery owing to its high theoretical energy density and sustainable components. An important challenge for research and development of chloride ion batteries lies in the innovation of the cathode materials. Here we report a nanostructured chloride ion-doped polymer, polypyrrole chloride, as a new type of potential cathode material for the chloride ion battery. The as-prepared polypyrrole chloride@carbon nanotubes (PPyCl@CNTs) cathode shows a high reversible capacity of 118 mAh g⁻¹ and superior cycling stability. Reversible electrochemical reactions of the PPyCl@CNTs cathode based on the redox reactions of nitrogen species and chloride ion transfer are demonstrated. Our work may guide and offer electrode design principles for accelerating the development of rechargeable batteries with anion transfer.

KEYWORDS: chloride ion batteries, cathode materials, electrochemistry, rechargeable batteries, polypyrrole chloride

INTRODUCTION

The chloride ion battery (CIB) is a new rechargeable battery based on Cl⁻ anion transfer. This battery shows diverse electrochemical couples with theoretical energy densities up to 2500 Wh L⁻¹, which is superior to those of conventional lithium ion batteries.¹ Abundant material resources such as Mg, Ca, Na, and metal chlorides (e.g., FeCl₃, CuCl₂, and MgCl₂) can be sustainable electrode candidates. High mobility and high reversibility of Cl⁻ anion was demonstrated in a battery system based on Mg²⁺/Cl⁻ transfer,² although Cl⁻ anion has a relatively high ionic radius.

The CIB includes a metal chloride/metal electrode system and an ionic liquid electrolyte allowing chloride ion transfer, as reported in the proof-of-principle study of CIB operated at room temperature.³ The problem is that the metal chloride cathode can react with chloride ions in the electrolyte by a Lewis acid/base reaction,¹,³ leading to the formation of soluble complex anion (e.g., FeCl⁵⁻ and CuCl⁴⁻), which could be electrochemically reduced to metal.⁴ This electrode dissolution and the subsequent shuttle would limit the use of metal chloride cathode in the liquid electrolyte system (see Figure S1). Metal oxychlorides with higher stability have been reported as new cathode materials for CIBs.⁵⁻⁹ Metal oxychloride/metal systems could also show high theoretical energy densities during the chloride ion transfer (see Figure S2). By carbon incorporation in the cathode or optimization of electrolyte composition, more than 70% of the theoretical discharge capacity of single-electron cathodes such as FeOCl and VOCl could be delivered.⁸,⁹ A preliminary study on the multielectron VOCl₂ cathode was also reported in the electrode system using VOCl as cathode and Mg/MgCl₂ composite as anode.⁷

Besides inorganic electrode materials in rechargeable batteries, organic electrode materials, in particular polymers, have been attracting much attention, due to their advantages of good electrochemical performance, high stability, abundant chemical elements (C, H, O, N, and S), structural tunability, and design flexibility.¹⁰⁻¹⁵ Conductive polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), and polyzacacene analogues showed electrochemical activities and have been studied as active materials or additives in the electrodes of alkaline metal ion batteries.¹⁶⁻¹⁹ Actually, both cation and anion can be doped in these compounds.²⁰⁻²³ In this work, we report a chloride ion-doped polymer, polypyrrole chloride (PPyCl), as a new type of potential cathode material for CIBs. Nanostructured PPyCl@carbon nanotubes (PPyCl@CNTs) composite material was prepared by chemical oxidative polymerization. The PPyCl@CNTs cathode showed reversible redox reactions based on chloride ion transfer, a high discharge capacity of 118 mA·h g⁻¹, and superior cycling stability.

EXPERIMENTAL SECTION

Synthesis of Materials. Multiwalled carbon nanotubes (Aladdin, >95%) were purified and oxidized in a mixture of concentrated
H₂SO₄/HNO₃ with a 3:1 ratio at 70 °C for 2 h under an ultrasonic condition. Then the carbon nanotubes were collected by removing excess acid and reaction byproducts via centrifugation and repeated washing with deionized water, followed by 12 h drying at 393 K under vacuum. Pyrrole monomer (Alfa Aesar, >98%) was purified before use by vacuum distillation at 343 K using a rotary evaporator. A 0.103 g amount of the as-prepared carbon nanotubes was dispersed in 70 mL of deionized water by sonication for 2 h. A 0.42 mL amount of the purified pyrrole monomer was then added via a syringe. Ten minutes later, 50 mL of 0.29 M FeCl₃·6H₂O (Aladdin, 99%) aqueous solution was added dropwise. The Fe³⁺/pyrrole molar ratio was 2.35. The polymerization was allowed to proceed for 4 h. All the procedures were carried out with constant sonication and Ar atmosphere protection under an ice bath condition. Afterward, the resulting black precipitate was vacuum-filtered and washed with deionized water until the washings were clear and neutral, followed by 24 h vacuum drying at 363 K. Pure polypyrrole chloride was prepared by the same procedures without the addition of carbon nanotube.

Structural Analysis and Electrochemical Tests. Measurements of X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transition electron microscopy (TEM, FEI Philips CM300 UT/FEG), and field-emission scanning electron microscopy were performed to characterize the structure, composition, and morphology. XPS curve fitting was performed using the standard nonlinear background subtraction and a Gaussian–Lorentzian ratio of 85:15. The composition (C, H, and N) of the as-prepared polypyrrole and...
polypyrrole chloride was obtained by using a Vario ELcube elemental analyzer. The BET surface area was calculated from nitrogen adsorption isotherms performed at 77 K using a BELSORP-Mini instrument. Fourier transform infrared spectroscopy (FTIR) was carried out with a Bruker Tensor 27 Infrared spectroscopy instrument. Coin cell assembling and discharge and charge testing in the range of 1−4 V were carried out as reported in our previous work. For the slurry coating of the cathode, PTFE (Aladdin, 60% in water) was used as a binder. The slurry was coated on stainless steel (SS) current collectors, pressed at 6 MPa, and dried under vacuum at 363 K for 24 h. The mass loading of the electrode materials ranged from 3.5 to 4.5 mg cm−2. Cyclic voltammetry (CV, 1 to 4 V, 50 μV s−1) and electrochemical impedance spectroscopy (EIS) 43 measurements were performed using a BioLogic (VMP3) electrochemical instrument.

RESULTS AND DISCUSSION

Figure 1 shows the structure and morphology analysis of the as-prepared PPyCl/CNTs nanocomposite. Polypyrrole chloride was uniformly and fully coated on the surface of the CNTs, resulting in an increase in the diameter from 10 to 30 to 40−80 nm and a decrease in the specific surface area from 221.8 to 190.3 m2 g−1 (see Figure S3). The result of EDS (see Figure S4) proves that chlorine was introduced into the as-prepared PPyCl@CNTs nanocomposite. TEM and HRTEM in Figure 1c and 1d show a more distinct coating morphology between PPyCl and CNTs, as indicated by the arrows. The PPyCl has a disordered structure, and the CNTs display clear lattice fringes. The scanning transmission electron microscopy (STEM) image and the corresponding element mapping images (Figure 1e) show a highly homogeneous distribution of C, N, and Cl in the as-prepared PPyCl@CNTs sample. The result of XRD in Figure 2a shows the characteristic peaks at around 25.8° and 42.7° corresponding to (002) and (100) lattice planes of the CNTs. The coating of PPyCl on the surface of the CNTs results in the formation of a broad diffraction peak overlapped with (002) plane of the CNTs. Only reflections of CNTs were observed by the selected area electron diffraction (SAED) image inset in Figure 2a. The amorphous structure of the as-prepared PPyCl was confirmed. This could be ascribed to the structural disorder by the formation of α−α′ (α-carbon) bonds coexisting with a small proportion of α−β (β-carbon) bonds in polypyrrole.24 Elemental analysis (EA) demonstrated that pure polypyrrole synthesized without the addition of the CNTs has a C:H:N mole ratio of 3.98:3.04:1, which is approximately the same as the theoretical value of 4:3:1. The CNTs ratio in the PPyCl/CNTs nanocomposite is calculated to be 17 wt % by EA. This value is very close to 18 wt % CNTs we added during synthesis according to the calculation by formation of the polymer product in reaction 1,24

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n(C_4H_7N) + 2.33nFeCl_3 \rightarrow [(C_4H_7N)_n + 0.33nCl]_n + 2.33nFeCl_2 + 2nhCl
\]

(1)

The result of Fourier transform infrared spectroscopy (FTIR) (see Figure S5) of the PPyCl/CNTs nanocomposite shows that the bands at 1622 and 1595 cm−1 correspond to C=C stretching vibrations.25 The region from 1470 to 1260 cm−1 is attributed to C=N stretching vibration in the ring. The band at 1237 cm−1 is related to C−H or C=N ring in-plane stretching. The C=C stretching in pyrrole ring is reflected at the region around 1104 cm−1.26 The band corresponding to the N−H and C−N in-plane deformation vibration is located at 1044 cm−1. Other characteristic bands assigned to the C−C out-of-plane ring deformation vibration (966 cm−1), the C−H out-of-plane deformation vibration (785 and 880 cm−1), and the C=C out-of-plane ring deformation or C−H rocking (678 cm−1) were also observed.27 XPS analysis was carried out to get further understanding of the as-prepared PPyCl structure. The survey (see Figure S6) and region spectra (Figure 2b−d) indicate the same elements as those detected by EDS. Figure 2b
shows that the C 1s peak is centered at 284.8 eV, which corresponds to the α–α′ bonds. The peak at 283.8 eV is assigned to α–β bonds. This indicates that the linkages in the as-prepared PPyCl@CNTs are mainly the α–α′ linkages. The peaks at 285.9 and 287.4 eV are mainly assigned to C=N/C=O and C=NC≡O bonds, respectively. The π−π* shakeup satellite C 1s components are located at higher binding level.25 The α–π* shakeup satellite C 1s components are located at higher binding energies.25 The N 1s peak in Figure 2c are fitted with four components centered at 397.7 (C≡N), 399.7 (–NH–), 401 (polaron, C=N′), and 402.5 (bipolaron, C=N′) eV. This is consistent with previous studies.28−30 The proportion of two types of positively charged nitrogen (N+/N = 0.33) in the as-prepared PPyCl@CNTs is an indication of the PPy doping level.25 The repeated unit in the as-prepared sample could be described as the formula of PPyCl0.33. Figure 2d shows the deconvolution of the Cl 2p region spectrum of the as-prepared PPyCl@CNTs sample. Three spin–orbit split doublets (Cl 2p3/2 and Cl 2p1/2) with Cl 2p3/2 peaks lying at about 197.2, 198.4, and 200.6 eV are obtained. The binding energy values at about 197.2 and 200.6 eV are due to the presence of ionic and covalent chloride species, respectively.26,31,32 The intermediate chlorine species is associated with anionic chloride species arising from the charge transfer interactions between the polypyrrole chain and the chloride ion.26,31−32

Figure 3 shows the discharge and charge profiles and CV patterns of the PPyCl/Li electrode system. The PPyCl@CNTs cathode shows an initial discharge capacity of 93 mAh g−1, which is 80% of the theoretical capacity of 115 mAh g−1 according to the doping level of 0.33 (PPyCl0.33), and a sloping discharge profile at the first cycle, as shown in Figure 3a. A large electrochemical polarization was also observed at the first cycle. After activation in the initial cycles, a maximum discharge capacity of 118 mAh g−1 was received (Figure 3c). The voltage gap between the discharge and charge was significantly decreased. Median voltage values of 2.4 and 3.2 V in the fifth discharge and charge were received, respectively. A discharge voltage plateau appears. Upon cycling a very slow capacity decay was noticed and more than 90 mAh g−1 reversible capacity was retained after 40 cycles. An increase in the Coulombic efficiency is also observed. This might be attributed to the fine nanostructure of the as-prepared PPyCl@CNTs sample and also the very low volume change less than 1% during the chlorine doping and undoping in polypyrrole.21 The first discharge and charge process in the CV pattern (Figure 3b) also shows a large polarization behavior, which is evidently reduced by a short activation. Then a distinct pair of redox peaks was observed. The reduction and oxidation peaks appear about 2.4 and 2.8 V, respectively. Upon cycling, the reversible redox reactions remain steady, which coincides with the result of discharge and charge in Figure 3a. The broad redox region may be due to the different chemical oxidation states of nitrogen and also diverse chlorine species in the as-prepared PPyCl@CNTs sample. Furthermore, a small rectangular shape area related to a capacitive contribution at high voltage above about 3.2 V is also included. The as-prepared PPyCl@CNTs cathode at the charged state can readily power commercial red light-emitting diode (LED) and white LED for more than 5 min in the soft-packing CIB or coin CIBs (Figure 3d and Figure S7), indicating that the PPyCl@CNTs nanocomposite as a new type of cathode materials for CIBs has great potential for practical applications in CIBs.

Figure 4 shows the XPS region spectra of N 1s in the PPyCl@CNTs cathodes at various electrochemical states and in the electrolyte of 0.5 M PP14Cl in PP14TFSI: (a) as-prepared, (b) first discharge, (c) first charge, (d) fifth discharge, (e) fifth charge, and (f) electrolyte. (g) Schematic illustration of the charge and discharge reactions of the conjugated PPyCl with α–α′ linkages.
probably due to that the reduction reaction is not fully reversible and/or the sample is partially oxidized by oxygen. The N⁺ species regarding to C–N⁺ was recovered by the subsequent charge at first cycle (Figure 4c), while the C=–N⁺ species was not fully recovered. Similar reduction and oxidation processes of N⁺ species were observed at the fifth cycle (Figure 4d and 4e), indicating the reversible electrochemical reactions of the as-prepared PPyCl@CNTs cathode during cycling. Upon cycling, the ratio of the intermediate anionic chloride species involved in the charge transfer interactions between the polypyrrole chain and the chloride ion increases (see Figure S9). Kang et al. demonstrated that this kind of chlorine species showed higher reactivity and was beneficial to enhance the electrical conductivity of PPyCl. EIS measurement was carried out for the PPyCl/Li electrode system before and after cycling, as shown in Figure S10. The electrochemical process of the PPyCl working electrode shows a mixed rate-determining step by charge transfer and chloride ion diffusion at high and low frequencies, respectively. Obviously the electrochemical resistance of the PPyCl cathode was reduced after cycling. This supported the result that the charge and discharge performance of the as-prepared PPyCl@CNTs cathode was evidently improved by the activation in initial cycles, as shown in Figure 3a.

Besides the chloride ion in the electrolyte, the PP14⁺ and TFSI⁻ are also included. The N 1s peaks of these two organic ions in the electrolyte are located at about 402.3 (N⁺) and 399.1 eV (N⁻), respectively, as shown in Figure 4f. On the basis of the results in Figure 4b–e, the bulky PP14⁺ and TFSI⁻ ions were not detected in the PPyCl@CNTs cathodes at the discharge and charge states, respectively. Actually, the electrochemical studies in the literature showed that the reduction of PPy could involve the intercalation of cations such as Li⁺, Na⁺, or K⁺ to form co-ions in the discharged PPY in aqueous or organic solution. This contribution by the cation was decreased when the cation size increased. The study using the Et₄NCl aqueous solution with a larger cation Et₄N⁺ showed that only Cl⁻ anion transport in PPyCl was observed by CV testing. Similar phenomena were also reported in the effect of secondary anion size on the electrochemistry of PPyCl, where the secondary anion with a larger size showed a lower contribution. Smyrl et al. reported that the PPy prepared with doping of small anions, medium size anions, and large size anions indicated only anion doping during the oxidation process, both anion and cation motions during the redox stage, and cation motion during the oxidation process, respectively. These phenomena were attributed to the sluggish diffusion of the bulky ions in the polymer matrix. Therefore, the chloride ion with a small size acts in the role of charge compensation of the oxidized sites in the discharged PPyCl@CNTs electrode during the charge process. The as-prepared PPyCl@CNTs cathode shows the dominant electrochemical reactions associated with chloride ion deintercalation/interaction during cycling, as illustrated by the charge and discharge of the conjugated PPyCl with dominant α–α' linkages in Figure 4g.

**CONCLUSION**

In summary, we developed the nanostructured chloride ion-doped polypyrrole as a new type of potential cathode material for the chloride ion battery. The as-prepared PPyCl@CNTs cathode had a high reversible capacity of 118 mAh g⁻¹ and superior cycling stability. The electrochemical polarization of the as-prepared PPyCl@CNTs cathode was decreased by the activation in initial cycles, which was probably associated with the increase of the intermediate anionic chloride species in the cathode during cycling. The result of XPS indicated that the reversible reaction of the as-prepared PPyCl@CNTs cathode was proved to be according to the chloride ion deintercalation/intercalation in PPyCl. This study provides opportunities to develop new cathode materials and also electrochemical systems for rechargeable batteries based on anion transfer.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b14755.

Schematic illustration of the dissolution and the subsequent shuttle of the metal chloride cathode in a liquid electrolyte. Energy densities of some electrochemical couples in rechargeable batteries. N₂ gas sorption isotherms, EDS spectrum, XPS survey spectrum, and Fe 2p region spectrum. Optical images of LED powered by coin CIB. XPS region spectra of Cl 2p before and after cycling. EIS patterns (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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