

University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2013

Polypyrrole as cathode materials for Zn-polymer battery with various biocompatible aqueous electrolytes

Sha Li

University of Wollongong, sl739@uowmail.edu.au

Irin Sultana

University of Wollongong, is988@uow.edu.au

Zaiping Guo

University of Wollongong, zguo@uow.edu.au

Caiyun Wang

University of Wollongong, caiyun@uow.edu.au

G G. Wallace

University of Wollongong, gwallace@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>



Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Polypyrrole as cathode materials for Zn-polymer battery with various biocompatible aqueous electrolytes

Abstract

Polypyrrole films doped with p-toluenesulfonic anions on stainless steel mesh substrates were prepared by the electropolymerization method. A Zn/aqueous solution/polymer battery system was thus established with the polymer film as the cathode and three different biocompatible aqueous electrolytes. The mechanism of the anode reaction can be explained as the dissolution of Zn. It was found, however, that the discharge performance, including the discharge plateaus and capacities, were significantly affected by the polymer reactions. To elucidate the reaction mechanisms of the conductive polymer, its electrochemical properties were systematically studied by several techniques, including cyclic voltammetry, electrochemical impedance spectroscopy, and monitoring mass changes with an electrochemical quartz crystal microbalance. The redox states of polypyrrole before and after discharge were investigated by Raman spectroscopy. The reaction mechanisms of the polypyrrole film and its effects on the discharge performance are thus discussed based on the results.

Keywords

electrolytes, aqueous, cathode, biocompatible, polypyrrole, various, battery, polymer, zn, materials

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Li, S., Sultana, I., Guo, Z., Wang, C., Wallace, G. G. & Liu, H. (2013). Polypyrrole as cathode materials for Zn-polymer battery with various biocompatible aqueous electrolytes. *Electrochimica Acta*, 95 212-217.

Authors

Sha Li, Irin Sultana, Zaiping Guo, Caiyun Wang, G G. Wallace, and Hua-Kun Liu

Polypyrrole as cathode materials for Zn-polymer battery with various biocompatible aqueous electrolytes

Sha Li^{a, c}, Irin Sultana^{a, c}, Zaiping Guo^a, Caiyun Wang^{b, c}, G.G. Wallace^{b, c}, Hua-Kun Liu^{a, c}

^a Institute for Superconducting and Electronic Materials, University of Wollongong

^b Intelligent Polymer Research Institute, University of Wollongong

^c Australia Research Council centre of Excellence for Electrochemical Materials

Abstract

Polypyrrole films doped with *p*-toluenesulfonic anions on stainless steel mesh substrates were prepared by the electropolymerization method. A Zn/aqueous solution/polymer battery system was thus established with the polymer film as the cathode and three different biocompatible aqueous electrolytes. The mechanism of the anode reaction can be explained as the dissolution of Zn. It was found, however, that the discharge performance, including the discharge plateaus and capacities, were significantly affected by the polymer reactions. To elucidate the reaction mechanisms of the conductive polymer, its electrochemical properties were systematically studied by several techniques, including cyclic voltammetry, electrochemical impedance spectroscopy, and monitoring mass changes with an electrochemical quartz crystal microbalance. The redox states of polypyrrole before and after discharge were investigated by Raman spectroscopy. The reaction mechanisms of the polypyrrole film and its effects on the discharge performance are thus discussed based on the results.

Keywords; Zn-polymer battery, Polypyrrole, Biocompatible, Simulated body fluid

Corresponding Author,
Professor Zai Ping Guo
Phone: +61 2 4221 5225
E-mail: zaiping_guo@uow.edu.au

1. Introduction

Biocompatible or implantable power sources have been a recent focus of research, based on the bloom of new bio-engineering techniques. Electrical energy is required for many such applications, including biosensors¹, growth control devices², artificial organs and nerves³ and⁴, telemetric readings, and monitoring⁵. Most such devices are operated under “in-vivo” circumstances, which need biocompatible batteries with a long service life.

Among all the types of bio-implantable power sources, one research direction has been to develop a biogalvanic cell with a steady discharge performance under low current density⁶. The concept of the biogalvanic cell has existed for decades: such a cell normally contains a sacrificial anode and a cathode with electrochemical activity. The metal-polymer battery system, such as the Mg/poly(3,4-ethylenedioxythiophene) (PEDOT) battery, has recently been regarded as a prospective candidate as a biocompatible power source⁷. Its mechanism has not been thoroughly studied, however. In this work, Zn was chosen as the anode due to its moderate corrosion rate in the aqueous solution and also its biocompatibility⁸. The anode reaction of the Zn-polymer battery is generally believed to be based on metal dissolution, which is much easier to explain than that of the polymer, since the interfacial reaction mechanism of zinc in aqueous solutions has been fully investigated^{8,9}. Meanwhile, to satisfy the safety demands, we chose polypyrrole (PPy) as the cathode material, due to its non-toxicity, stability, and other predominant advantages such as high conductivity and redox reversibility^{10,11}. Its reaction mechanism has not been fully investigated, although the redox process in conductive polymers and their role in the battery are of high complexity, which demands further exploration.

Three types of neutral aqueous electrolytes were chosen: NaCl solution, phosphate buffered saline (PBS) solution, and simulated body fluid (SBF). They are all non-toxic electrolytes, which are ideal for biocompatible batteries. The discharge performances varied among the batteries with different electrolytes. This phenomenon also evokes the research interest in tracing the

relationship between the discharge performance and the reactions in polypyrrole films. The Zn-polypyrrole battery has rarely been reported, especially the Zn-PPy batteries using bio-compatible electrolyte. The Zn-polypyrrole batteries exhibit large discharge capacity at low current rate, which makes them a suitable candidate power source for certain applications, such as implantable devices.

1.1 Experimental Methods

1.1.1 Preparation of electrolyte

Three types of electrolyte were prepared for battery construction: 0.1 M NaCl solution, phosphate buffered saline (PBS) solution, and simulated body fluid. The PBS solution was prepared by dissolving one PBS tablet in 200 ml de-ionized water. The ion concentrations of the PBS buffer electrolyte and the SBF are listed in table 3.1. All chemicals were purchased from Sigma–Aldrich and used as received.

Table 0.1 Ion concentrations in SBF and PBS buffer electrolytes.

	Ion concentrations (M)	
	PBS buffer	SBF
Na ⁺	0.167	0.142
K ⁺	0.0027	0.005
Mg ²⁺	–	0.00153
Ca ²⁺	–	0.00264
Cl ⁻	0.1357	0.102
H ₂ PO ₄ ⁻	0.01	–
HPO ₄ ⁻	0.01	0.001

	Ion concentrations (M)	
	PBS buffer	SBF
OH ⁻	–	0.02
HCO ₃ ⁻	–	0.006
CO ₃ ²⁻	–	0.004
SO ₄ ²⁻	–	0.0005
HEPES	–	0.075

1.1.2 Electro-deposition of polypyrrole films

Polypyrrole films were electrochemically deposited on stainless steel mesh substrate in an aqueous solution containing 0.1 M freshly distilled pyrrole monomer and 0.1 M *p*-toluenesulfonic acid sodium salt (*p*TSNa). The solution was deoxygenated by nitrogen gas for 30 min before deposition. The polypyrrole films were polymerized under a constant current of 0.5 mA cm⁻² for 30 min¹².

1.1.3 Battery assembly

Pieces of 1 mm thick Zn foil were cut into squares 1 cm × 1 cm in size and then polished mechanically to remove the oxidation layers. Both the Zn square and the polypyrrole film were immersed in the electrolyte. The areas of both electrodes were restricted to 1 cm².

1.1.4 Characterization methods

The growth in weight of the polypyrrole film was monitored in situ by an electrochemical quartz crystal microbalance (EQCM). The thickness and surface morphology were measured using an atomic force microscope (AFM, Asylum Research MFP-3D). Raman spectroscopy was carried out to characterize the redox state of the polypyrrole film before and after discharge, using a

JOBIN YVON HR800 Confocal Raman system with 632.8 nm diode laser excitation on a 300 lines/mm grating at room temperature.

The discharge tests were carried out with a battery testing device (Land CT2001A, Wuhan Jinnuo Electronics Co. Ltd), which was interfaced to a computer with software allowing the discharge process to stop at the pre-set cut-off potentials. The cells were discharged from the open circuit potential to 0.7 V with a discharge rate of $40 \mu\text{A mg}^{-1}$. Electrochemical impedance spectroscopy (EIS) was performed using a CHI 660C electrochemistry workstation. The ion exchange behavior of the polymer films was characterized in the corresponding electrolyte applied for cell construction by EQCM.

1.2 Results and discussion

1.2.1 Properties of polypyrrole films

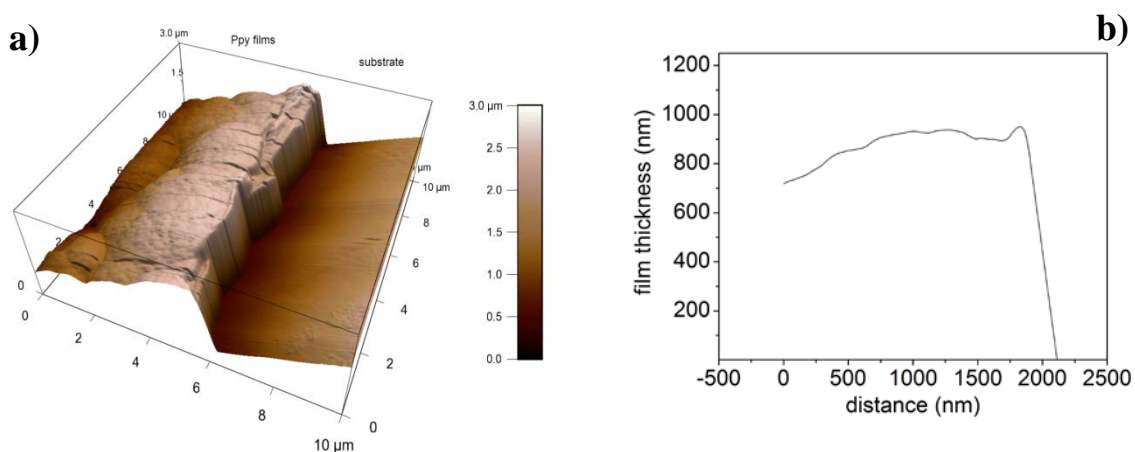


Figure1. AFM image of *p*TS doped PPy film (a), and the film thickness measured along the film profile (b).

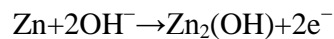
A polypyrrole film was deposited on a gold coated quartz crystal under the same conditions as for the electrodes used for battery construction. The mass change was observed in situ by converting the change in frequency of the quartz crystal resonator. The mass of polypyrrole increased

linearly during the deposition period, which indicated that the conductive film grew normally with the sulfonate doping¹³. The film conductivities were measured by a four-probe detector, and the average value was calculated to be 70 S m^{-1} .

Atomic force microscope images were obtained within a region of $10 \mu\text{m} \times 10 \mu\text{m}$ (Fig. 3.1) to investigate the surface morphology and thickness of the polypyrrole film deposited on the gold coated quartz crystal. The thickness of the film is less than $1 \mu\text{m}$, as shown in Fig 3.1(b). The ultra-thin films have less charge transfer resistance and thus allow much easier ion-exchange with the electrolyte than the thicker ones¹⁴.

1.2.2 Battery discharge

Fig. 3.2(a) presents the discharge curves of the Zn/aqueous electrolyte/PPy batteries, which showed very high capacities calculated according to the mass of polypyrrole. The anode reaction can be identified as interfacial dissolution and oxidation of the Zn foil which can be concluded to obey the redox equation below



At the beginning of the discharge, an insoluble thin layer of zinc hydroxide is formed on top of the zinc electrode, which causes a sharp potential drop. Zinc dissolution, however, will also cause the pH of the electrolyte to decrease and thus stimulates the dissolution of the insoluble zinc hydroxide¹⁵. As can be seen from Fig.3.2, the discharge plateau of the Zn/NaCl/PPy battery lasts longer than for the cells using the other two electrolytes, although there is a sharper potential drop at the beginning of discharge. Also, the battery open circuit potentials (OCPs) are in a descending order of NaCl (1.16 V) > PBS (1.09) > SBF (1.02 V).

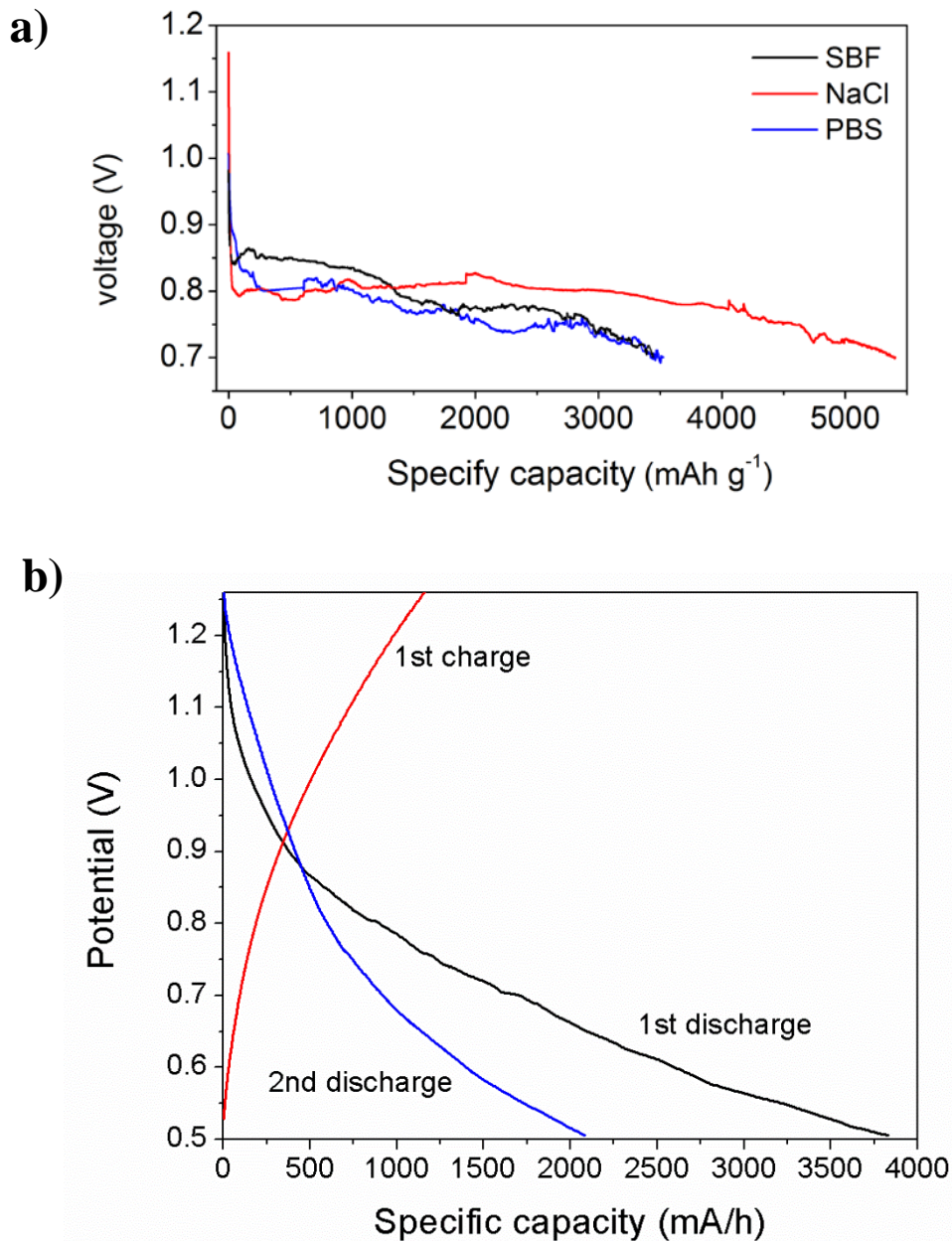


Figure.2 (a) Discharge curves of Zn/PPy batteries ($40 \mu\text{A mg}^{-1}$) with different electrolytes: simulated body fluid (black line), 0.1 M NaCl (red line), PBS buffer solution (blue line); (b) the 1st charge and the 2nd discharge curves of Zn/PPy batteries in SBF electrolyte ($160 \mu\text{A mg}^{-1}$).

If the mechanism of the battery is simply explained as the redox reactions between the Zn foil and the polypyrrole film, there is definitely not enough polypyrrole to be reduced and thus maintain the long discharge plateaus. This means that the cathode reaction cannot be simply explained as the reduction of conductive polymer. Not much evidence has ever been provided to investigate the role of polypyrrole in batteries. In order to understand the reversibility of the Zn/PPy batteries,

the cells with SBF as electrolyte were charged and discharged at a current density of $160 \mu\text{A mg}^{-1}$ for another cycle (as shown in Fig. 3.2(b)). It can be seen that the Zn/PPy batteries delivered a reversible capacity of more than 2000mAh g^{-1} , suggesting its great potential as biocompatible power sources in the real applications. Fig 3.3 presents the polarization behaviour of Zn electrodes after immersion for 72 h in the three electrolytes. The corrosion potential of Zn in NaCl solution is higher than in the PBS buffer, implying that the Zn dissolution is easier in the PBS buffer. If the discharge properties are only correlated to the redox reaction on the Zn foil, the battery with PBS buffer electrolyte should have higher capacity than the others, which is untrue according to the discharge curves. This indicates that the battery properties must also be affected by the reactions of the polypyrrole. In order to elucidate the functions of the polypyrrole film, both the electrochemical properties and its redox states before and after discharge are discussed in the following part.

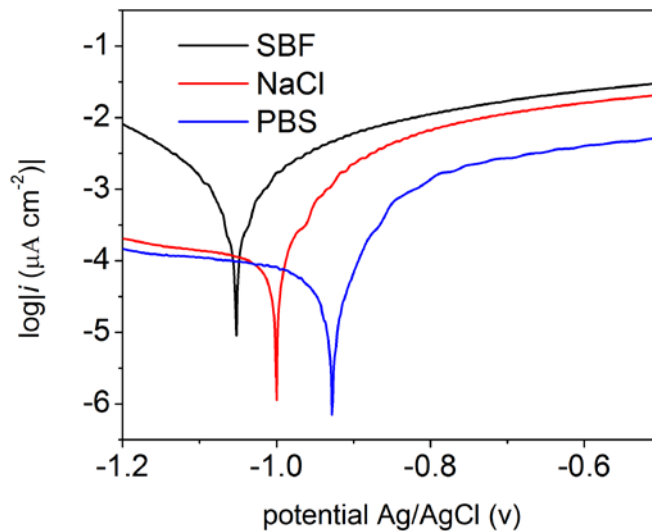


Figure.3 Polarization curves of Zn electrodes in different electrolytes: simulated body fluid (black line), 0.1 M NaCl (red line), and PBS buffer solution (blue line).

1.2.3 Electrochemical properties of polypyrrole electrode

Polypyrrole with pTS^- counterions (PPy/ pTS^-) was investigated in different electrolytes by cyclic voltammetry (Fig 3.4) to evaluate the redox characteristics and the charge storage capacities of the electrodes. The thicknesses of the polymer films used for cyclic voltammetry (CV) testing are similar, since the films were deposited under the same conditions. The electrodes were scanned between -1.0 V and 0.3 V (vs. Ag/AgCl) to prevent over oxidation or insulation of the film¹⁶⁻¹⁸. The oxidation potentials of the films in the three electrodes are at around -0.2 V, however, it is obvious that the peak currents of the PPy films in the NaCl and PBS electrolytes are relatively higher than in SBF, and there are no obvious reduction peaks of polypyrrole in SBF, while the polypyrrole films in both the NaCl and the PBS have a reduction peak at around -0.6 V, which suggests that the film in SBF has less capacity and reversibility. The relevant reduction and oxidation mechanisms of the PPy electrodes are shown in Scheme 3.1.

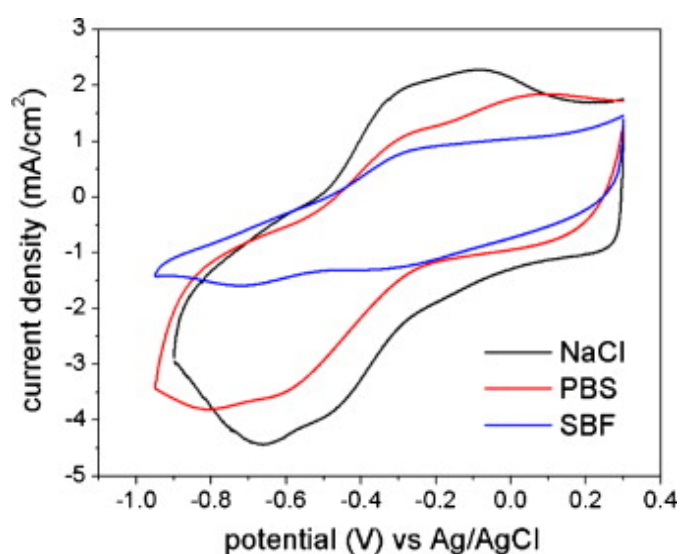
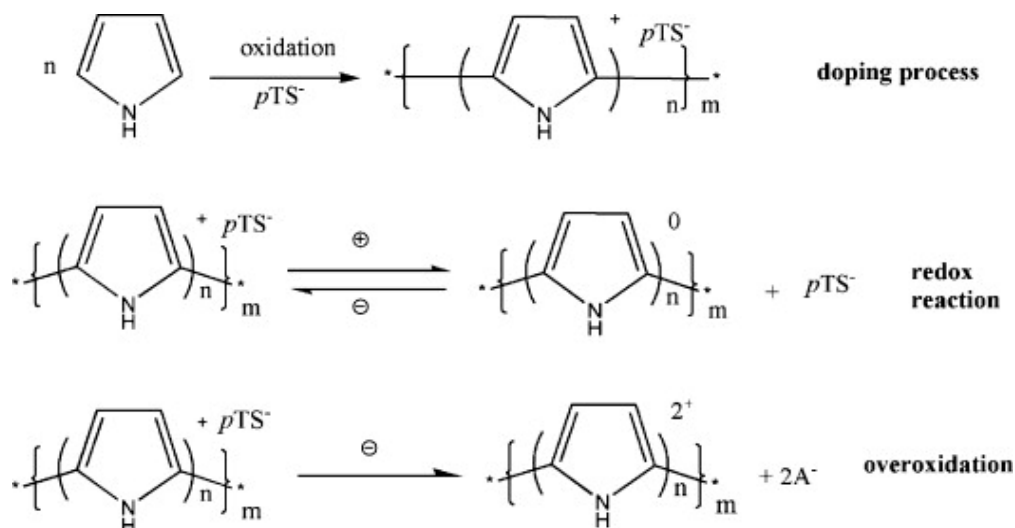


Figure.4 Cyclic voltammetric response of (PPy/ pTS^-) in different electrolytes: PBS buffer solution, 0.1 M NaCl, and simulated body fluid; scan rate = 10 mV/s.



Scheme.1 Reduction and oxidation reactions of the PPy films.

The mass change curves converted from the EQCM response are shown in Fig 3.5. Since pTS^{n-} is a large counterion, the ion exchange mechanism of polypyrrole can be mainly ascribed to the cation exchange model^{19, 20}. During reduction, the mass increase of PPy/ pTS^{n-} is caused by the absorption of cations in the electrolyte so as to neutralize the anionic sulfonyl groups of the pTS^{n-} counterions, while the mass decrease during the oxidation is due to the desorption of cations. The curves in Fig 3.5 reveal that the ion exchange of polypyrrole film in the NaCl solutions is much more violent than in the other electrolytes. This is mainly because the NaCl solution only contains chloride ions, which are univalent small counterions and have little effect on the ion mobilities of Na^+ ions. Thus, the Na^+ ions can be easily inserted into or expelled from the polymer and participate in the redox reaction. Both the SBF and PBS buffer electrolytes contain large amounts of large counterions or organic moleculars ($H_2PO_4^-$ in PBS buffer or 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) in SBF), which could retard the ion migration.

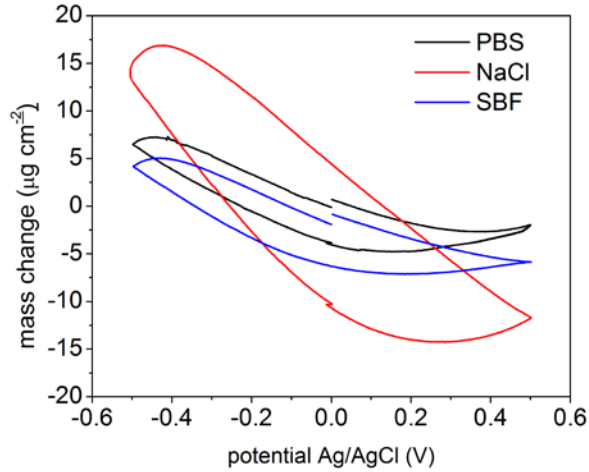


Figure.5 Mass change converted from the EQCM frequency response in different electrolytes: PBS buffer solution (black line), 0.1 M NaCl (red line), and simulated body fluid (blue line).

The polymer films were also investigated using electrochemical impedance spectroscopy (EIS) before and after discharge (Fig 3.6 (a) and (b)). Two well-separated patterns were observed: an arc was obtained at high frequencies, which is related to the metal/polymer and polymer solution interface charge transfer processes, while the lines in the low-frequency region indicate capacitive behaviour related to the film charging mechanism. The difference in the real part of the impedance between low and high frequencies could be used to evaluate the value of the electrochemical charge transfer resistance (R_{ct})²¹.

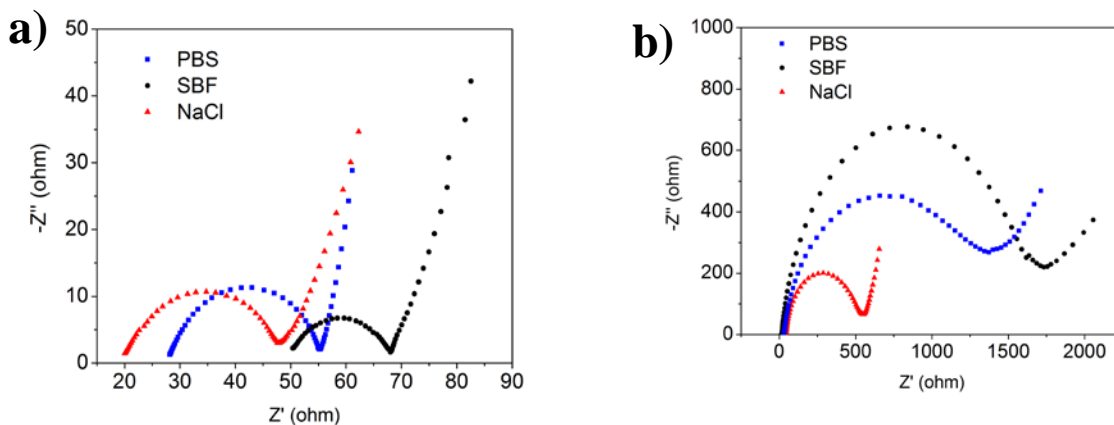


Figure.6 Impedance plots of the PPy electrodes in different electrolytes (a) before discharge, and (b) after discharge.

The charge transfer resistance of the films immersed in different electrolytes was calculated as 27.439 ohm (NaCl), 27.35 ohm (PBS), and 19.654 ohm (SBF), respectively. The cells with NaCl and PBS electrolytes have almost the same Rct, while the Rct value for the cell with SBF as electrolyte is lower. After discharge (72 h), however, the Rct of the cell with NaCl solution as electrolyte (432.89 Ω) is much lower than for the others. The higher charge transfer resistance of the cells using PBS or SBF as electrolyte compared to those using NaCl, may due to the absorbed larger HPO_4^{2-} , H_2PO_4^- , and HEPES species on the surface of electrodes, which blocked the ion diffusion to some extent.

The redox kinetics of polypyrrole films is mainly controlled by the ion-exchange and charge transfer processes²². Since the PPy film has both a faster ion-exchange rate and smaller charge transfer resistance in NaCl solution, the redox activities are higher. Therefore, the discharge capacities of Zn/NaCl/PPy batteries are larger than for the batteries containing the other two electrolytes. The CV curves in Fig 3.5 reveal that the PPy films have similar redox reactivity in both the PBS buffer and the SBF solution. The discharge capacities of batteries with PBS buffer electrolyte, however, are much lower than for the ones with NaCl electrolyte, similar to the case of the Zn/SBF/PPy battery. This is due to the fact that the resistances in both the ion-exchange and charge transfer processes are much larger in the PBS buffer than in the NaCl solution.

1.2.4 Redox states of polypyrrole before and after discharge

Since it has been proved that both the redox kinetics and the associated reactivity have effects on the discharge capacities, it is quite necessary to find out the exact redox process of the polypyrrole films. It is obvious that the reduction of polypyrrole is not the main contributor to the high capacities. The polypyrrole film would lose its conductivity if it were fully reduced and cause the inactivation of the battery. In previous research work, the genuine cathode reaction was explained as oxygen reduction^{7, 23}. No evidence has ever been provided, however, about the redox

states of the polypyrrole films before and after discharge, which is the direct proof for elucidating the reaction mechanism.

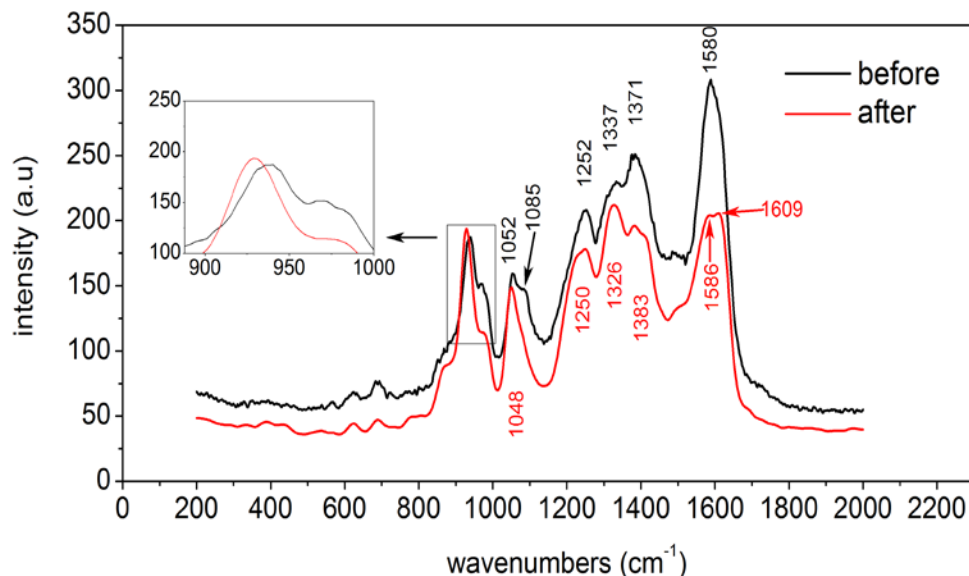


Figure 0.7 Raman spectra of PPy/pTS film before and after battery discharge in SBF. The inset is an enlargement of the indicated region.

The redox states of polypyrrole before and after discharge were studied by Raman spectroscopy (Fig.3.7). The peak at around 930 cm^{-1} can be assigned to the symmetric stretching mode of the counter ions. It is always accompanied by a broad shoulder on the high frequency side, which is assigned to the incorporated salts²⁴. These two vibrational peaks coexist, indicating that the film both before discharge and after discharge is a mixture of polaron and bipolaron polypyrrole. The 980 cm^{-1} band (the broad shoulder at around 930 cm^{-1}) indicates that certain sites on the PPy chain are still in the benzoid form (reduced state). The vibrational mode at 930 cm^{-1} , assigned to a C-H out-of-plane deformation of the quinoid form, is related to the oxidized sites²⁵. The PPy film before discharge clearly has a double peak at about 1052 and 1085 cm^{-1} , which can be assigned to the C-H in-plane deformation of oxidized PPy. In contrast, there is only one peak at 1048 cm^{-1} for the discharged sample, which indicates that the film also contains the fully reduced species. The bands in the high frequency region around 1600 cm^{-1} correspond to the backbone

stretching of C=C bonds, and their intensity is correlated to the polymer conductivity²⁵⁻²⁷. The peak intensity of the PPy film after discharge in this region is significantly lower than for the film before discharge, implying that the film partially loses its conductivity after the discharge process²⁷.

According to the analysis of the Raman spectra above, the PPy electrodes were partially reduced after discharge, staying in an intermediate state which contains both the reduced and the oxidized forms. Accordingly, the film is not likely to be fully reduced and then oxidized in an orderly way. This means that there are reversible redox reactions that arise on the polymer, as showed in Fig 3.8. The redox reversibility and ultra-high ionic mobility of polypyrrole in these aqueous electrolytes make it clear that its redox reaction is a simultaneous bidirectional process. Polypyrrole can act as an oxygen consumer and thus accelerate the oxygen dissolution. At the same time, it can also be reduced and incorporated with Zn^{2+} , which helps to maintain the zinc dissolution rate.

Conclusions

The electrochemical properties and reaction mechanism of the Zn/bio fluids /polypyrrole battery has been investigated. The role of polypyrrole film in the battery can be concluded as both that of an oxygen consumer, which can catalyse the oxygen dissolution, and that of an electron acceptor, which helps to maintain the Zn dissolution rate. Both the capacitance and the ion-exchange capability of the PPy films in different electrolytes affect the discharge performance. Higher values of polymer capacitances and ion-exchange rates induce higher capacities. Based on this understanding of such mechanisms, further modifications of the polymer electrodes can be carried out, which is essential for developing biocompatible batteries with non-toxic aqueous electrolytes.

1. A. Vaseashta and D. Dimova-Malinovska, *Science and Technology of Advanced Materials*, 2005, **6**, 312-318.
2. R. D. Dell, J. C. Gord and J. H. Schulman, Google Patents, 2000.
3. M. Haugland, A. Lickel, J. Haase and T. Sinkjær, *Rehabilitation Engineering, IEEE Transactions on*, 1999, **7**, 215-227.
4. N. R. Hagfors, Google Patents, 1974.
5. N. Bandeira, C. Gastouniotis, B. E. Gray and S. H. Seehoffer, Google Patents, 1995.
6. J. Rao and G. Richter, *Naturwissenschaften*, 1974, **61**, 200-206.
7. B. Winther-Jensen, M. Gaadingwe, D. Macfarlane and M. Forsyth, *Electrochimica Acta*, 2008, **53**, 5881-5884.
8. C. Cachet and R. Wiart, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 1981, **129**, 103-114.
9. X. G. Zhang, *Corrosion and electrochemistry of zinc*, Springer, 1996.
10. N. K. Guimard, N. Gomez and C. E. Schmidt, *Progress in Polymer Science*, 2007, **32**, 876-921.
11. B. Grgur, M. Gvozdenović, J. Stevanović, B. Jugović and V. Marinović, *Electrochimica Acta*, 2008, **53**, 4627-4632.
12. A. Diaz, K. K. Kanazawa and G. P. Gardini, *Journal of the Chemical Society, Chemical Communications*, 1979, 635-636.
13. P. Christensen and A. Hamnett, *Electrochimica Acta*, 1991, **36**, 1263-1286.
14. X. Ren and P. G. Pickup, *Journal of Electroanalytical Chemistry*, 1997, **420**, 251-257.
15. L. Baugh, *Electrochimica Acta*, 1979, **24**, 657-667.
16. C. Hsueh and A. Brajter-Toth, *Analytical Chemistry*, 1994, **66**, 2458-2464.
17. D. Ofer, R. M. Crooks and M. S. Wrighton, *Journal of the American Chemical Society*, 1990, **112**, 7869-7879.
18. T. Osaka, T. Momma, S.-i. Komaba, H. Kanagawa and S. Nakamura, *Journal of Electroanalytical Chemistry*, 1994, **372**, 201-207.
19. C. Weidlich, K.-M. Mangold and K. Jüttner, *Electrochimica Acta*, 2005, **50**, 1547-1552.
20. R. Ansari Khalkhali, W. Price and G. G. Wallace, *Reactive and Functional polymers*, 2003, **56**, 141-146.
21. J. R. Scully, D. C. Silverman and M. W. Kendig, *Electrochemical impedance: analysis and interpretation*, ASTM International, 1993.
22. L. Yongfang and Q. Renyuan, *Journal of Electroanalytical Chemistry*, 1993, **362**, 267-272.
23. Y. Kong, C. Wang, Y. Yang, C. O. Too and G. G. Wallace, *Synthetic Metals*, 2012, **162**, 584-589.
24. Y.-C. Liu, B.-J. Hwang, W.-J. Jian and R. Santhanam, *Thin Solid Films*, 2000, **374**, 85-91.
25. M. Santos, A. Brolo and E. Girotto, *Electrochimica acta*, 2007, **52**, 6141-6145.
26. Y.-C. Liu and B.-J. Hwang, *Synthetic Metals*, 2000, **113**, 203-207.
27. C. Zhong, Z. Tian and Z. Tian, *Journal of Physical Chemistry*, 1990, **94**, 2171-2175.