

Short communication

# Novel electrode substrates for rechargeable lithium/polypyrrole batteries

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## Abstract

A lightweight and inexpensive stainless steel mesh has been investigated as an electrode substrate material for Li/polypyrrole rechargeable battery. The effects of substrate materials on surface morphology of films, charge–discharge capacity and coulombic efficiency are discussed in detail. The results show that the capacity of the cell with stainless steel mesh is about 10% lower than the cell using platinum mesh, but it is much lighter and cheaper than that of platinum mesh, therefore, it is a promising substrate material for Li/polymer batteries.

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## 1. Introduction

In recent years, many different types of electroactive conducting polymers have been synthesized [1]. Among these polymers, conducting polypyrroles have drawn the most attention due to their superior electroactivity, good electrical conductivity and chemical stability. Owing to their physical, chemical and electrochemical properties, polypyrroles have been applied in many different fields including sensors [2], cable shielding [3], ion-selective membranes [4] and electrocatalysis [5–7]. Very recently, the application of polypyrrole as cathode material for rechargeable batteries has also been reported [8–10].

Fabrication of conducting polymer electrodes involves the use of a conductive substrate. To date, platinum foil is almost exclusively used as the electrode substrate for polymer based batteries [11–13]. Despite good performance, the use of a platinum substrate may never become a practical choice due to cost. In order to select a commercially available substrate material for commercial polymer batteries, lightweight and inexpensive stainless steel mesh was chosen and inves-

tigated as substrate material in this work. To the best of our knowledge, there has been no report on the use of stainless steel mesh as the substrate for fabrication of polymer based battery. In this work, the performance characteristics of the polypyrrole-based batteries using stainless steel mesh as the substrate electrode were evaluated by comparison with batteries constructed using platinum mesh.

## 2. Experimental

### 2.1. Reagents and materials

Propylene carbonate (Aldrich) and  $\text{LiClO}_4$  (Aldrich) used for preparing polypyrrole electrodes were both of RG grade and used as received. The  $\text{LiClO}_4$  used for electrolyte of cell testing was vacuum-dried at about  $100^\circ\text{C}$  for 24 h. Pyrrole monomer from Merck was distilled and stored below  $-18^\circ\text{C}$  before use. Silver nitrate (BAS), tetrabutylammonium perchlorate (TBAP, Fluka) and acetonitrile (APS) were used as received.

Two types of materials, platinum mesh (Engelhard-Clal Australia Pty Ltd.) and stainless steel mesh (Metal Mesh Pty Ltd., Australia), were used as electrode substrates for fabrication of polymer electrodes.

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## 2.2. Preparation of polypyrrole electrodes

All experiments were carried out using a three-electrode electrochemical cell. The potential required for polymerization and chronoamperometry was applied using an EG&G Princeton Applied Research (PAR) Model 363 potentiostat/galvanostat. A BAS CV-27 voltammograph was employed for cyclic voltammetry. The data was processed and recorded by a MacLab/4e (ADI Instruments) interfaced with a computer. The reference electrode was Ag/Ag<sup>+</sup> (in 0.01 M AgNO<sub>3</sub>, 0.1 M TBAP/CH<sub>3</sub>CN).

### 2.2.1. Cyclic voltammetry and chronoamperometry

Using platinum mesh or stainless steel mesh, cyclic voltammetry was performed by scanning the potential between 0 and 0.8 V at a rate of 100 mV s<sup>-1</sup>. The electropolymerization solution contained 0.16 M pyrrole and 0.75 M LiClO<sub>4</sub> in propylene carbonate (PC).

Chronoamperometry was then performed for 2 min at applied potentials of +0.5, +0.6, +0.7, +0.8 and 0.9 V. From these data, the conditions for preparing the polypyrrole electrode for batteries were selected.

### 2.2.2. Electropolymerization

The conducting polypyrrole electrodes were fabricated by a single-step electropolymerization of polypyrrole onto platinum mesh (30 mm × 70 mm × 1.5 mm) or stainless steel mesh (30 mm × 70 mm × 1.5 mm). Polymer samples were grown by electropolymerization from a solution of 0.16 M pyrrole, 0.75 M LiClO<sub>4</sub> in propylene carbonate (PC) at 0.75 V (versus Ag/Ag<sup>+</sup> in 0.01 M AgNO<sub>3</sub>, 0.1 M TBAP/CH<sub>3</sub>CN) to a total deposition charge density of 12.5 C cm<sup>-2</sup>. Following electropolymerization, these electrodes were dried in a vacuum oven for 24 h at room temperature, then cut to a small size of 1 cm<sup>2</sup> and transferred to an argon-filled glove box. The weight of polymer was about 6 mg. The dried electrodes were assembled into cells and were tested.

## 2.3. Conductivity measurement

The resistance measurements of the substrates and polypyrrole electrodes were performed on long strips using the ASTM four-probe technique. A DC current of 0.5 mA was applied across the two electrodes using an EG&G PAR 363 and the voltage drop across the two inner electrodes was measured using a HP multimeter (Model 34401A).

## 2.4. Cell assembly and testing

A polypropylene microporous separator was used in the cells. The separator was sandwiched between the two electrodes. The electrolyte used was 0.5 M LiCO<sub>4</sub> dissolved in PC. The electrolyte solution was dried several weeks over molecular sieves to reach less than 20 ppm of water content. Lithium foil of 300 μm thickness and area of 0.78 cm<sup>2</sup> was used as the negative electrode. Cells were assembled in an

argon-filled glove box (Unilab, Mbraun, USA) with both water and oxygen concentrations less than 5 ppm.

Charge/discharge tests were carried out by using a battery testing device (Neware, Electronic Co., China) interfaced to a computer with software. The system is capable of switching between charge and discharge automatically according to the pre-set cut-off potentials. The cells were cycled between 2.5 and 4.3 V with a constant current of 0.1 mA cm<sup>-2</sup>.

## 2.5. Electrochemical AC impedance analysis

Impedance analysis was conducted using a conventional three-electrode configuration. Polypyrrole electrodes were used as the working electrode. Lithium foils were used as both counter and reference electrodes. The impedance was measured with an EG&G Model 6310 Electrochemical Impedance Analyzer (Princeton Applied Research) run by Model 398 software within a frequency sweep range of 10 000 kHz–0.01 Hz.

## 2.6. Scanning electron microscopy (SEM)

Morphologies of the electrodes were examined using a Leica Model Stereoscan 440 scanning electron microscope manufactured in the UK. SEM examinations were carried out at room temperature under an accelerating voltage of 20 kV.

# 3. Results and discussion

## 3.1. Physical properties of substrates

Since a major function of the substrate is to be a collector for current during charge and discharge reactions in a battery, the conductivity of the substrate is one of the most important parameters in selecting electrode substrates. The conductivity of the test substrates investigated here was measured (Table 1). The platinum mesh and the stainless steel mesh all show good conductivity with the conductivity of the platinum mesh more than double that of the stainless steel mesh.

Non-reactive components add to the weight and volume of the battery [14]. Therefore, reducing the weight of the non-capacity contributing components, such as substrate, can improve the specific energy of the batteries [15,16]. The weights of the tested substrates in this work are listed in Table 1. The weight of the stainless steel mesh is just about one quarter of the weight of the platinum mesh. So using lightweight

Table 1  
Physical properties of tested substrates

| Substrate            | Conductivity (S cm <sup>-1</sup> ) | Weight (mg cm <sup>-2</sup> ) |
|----------------------|------------------------------------|-------------------------------|
| Platinum mesh        | 6.8 × 10 <sup>3</sup>              | 62.3                          |
| Stainless steel mesh | 3.1 × 10 <sup>3</sup>              | 16.8                          |

substrates of stainless steel mesh will improve the specific energy of a battery.

### 3.2. Electrochemical deposition of polypyrrole

In this study, platinum or stainless steel mesh was employed as the working electrode and polypyrrole was electrochemically deposited on them. In order to select a suitable polymerization potential, cyclic voltammetric experiments were performed. The cyclic voltammograms at both platinum and stainless steel substrate electrodes were obtained in a polymerization solution containing 0.16 M of pyrrole and 0.75 M of  $\text{LiClO}_4$  as the electrolyte in PC using a scan rate of  $20 \text{ mV s}^{-1}$  (see Fig. 1). During the anodic potential scan, a sharp increase in oxidation current was observed in its first cycle at around 0.50 V versus  $\text{Ag}/\text{Ag}^+$  when using the platinum electrode (Fig. 1a). A more gentle increase in oxidation current was observed at a much lower potential (0.35 V) in subsequent cycles. This is because a much higher oxidation potential is required for deposition of polypyrrole on the bare substrate while a lower potential is needed during the polymer propagation [17]. Similarly, a higher oxidation potential

of around +0.60 V versus  $\text{Ag}/\text{Ag}^+$  is required during the initial formation of polypyrrole on a stainless steel mesh in the first cycle (Fig. 1b), while the same lower potential of 0.35 V is needed during the subsequent growth of polypyrrole.

Chronoamperometric experiments were subsequently performed in a solution containing 0.16 M pyrrole and 0.75 M  $\text{LiClO}_4$  in PC. The chronoamperometric responses observed during polypyrrole growth on stainless steel mesh and platinum mesh are shown in Fig. 2. Fig. 2a shows the chronoamperometric responses of the stainless steel mesh substrate electrode. When a potential of +0.50 V was applied, low anodic current was obtained indicating low polymerization efficiency. With the applied potential of +0.60 V, a transient was observed initially due to the charging current. This was followed by a rapid increase in the current that then levelled off. The current increase observed was due to the increase of effective electrode surface area as a result of the deposition of conducting forms of polypyrrole. When the applied potential was greater than +0.8 V, the characteristics of the current responses observed were different to that observed with low applied potentials. The current decreased after reaching a maximum rather than leveling off. This is due to the increase in the electrical resistance caused by over-oxidation, since the

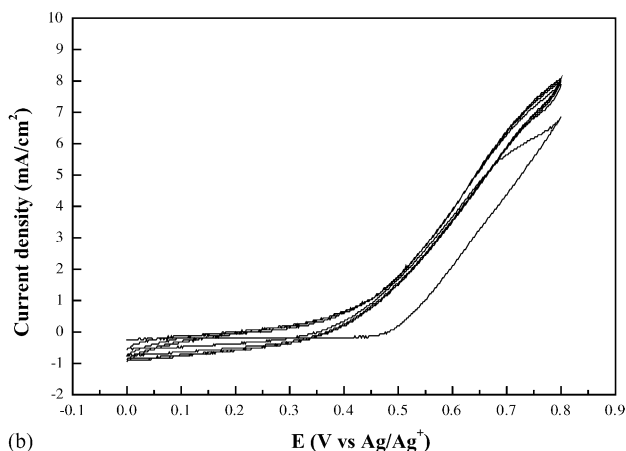
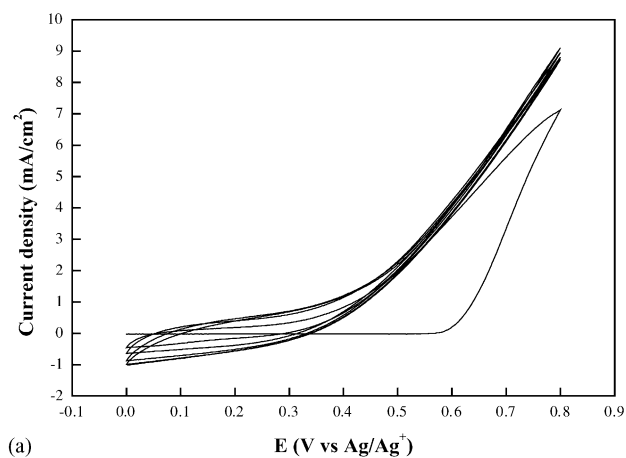


Fig. 1. Cyclic voltammograms obtained in 0.16 M pyrrole in 0.75 M  $\text{LiClO}_4/\text{PC}$  at different substrates: (a) platinum mesh and (b) stainless steel mesh.

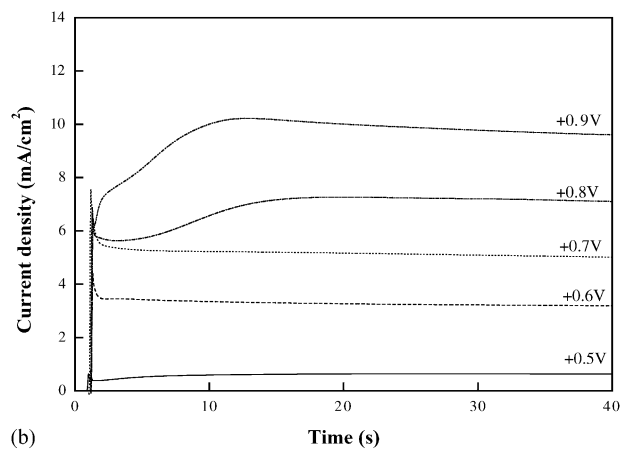
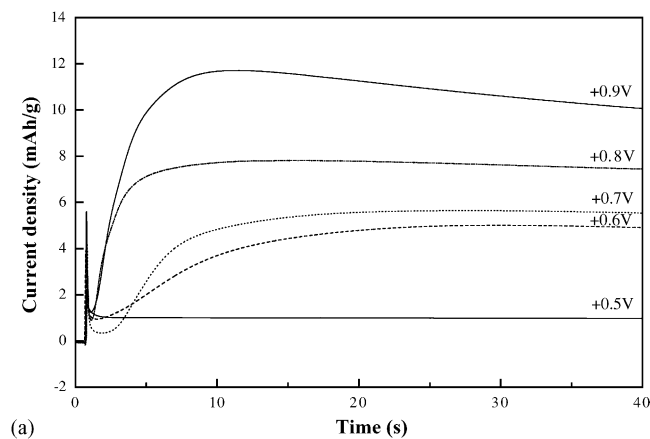


Fig. 2. Chronoamperometric response at different potentials for oxidation of 0.16 M pyrrole in 0.75 M  $\text{LiClO}_4/\text{PC}$  at different substrates: (a) stainless steel mesh and (b) platinum mesh.

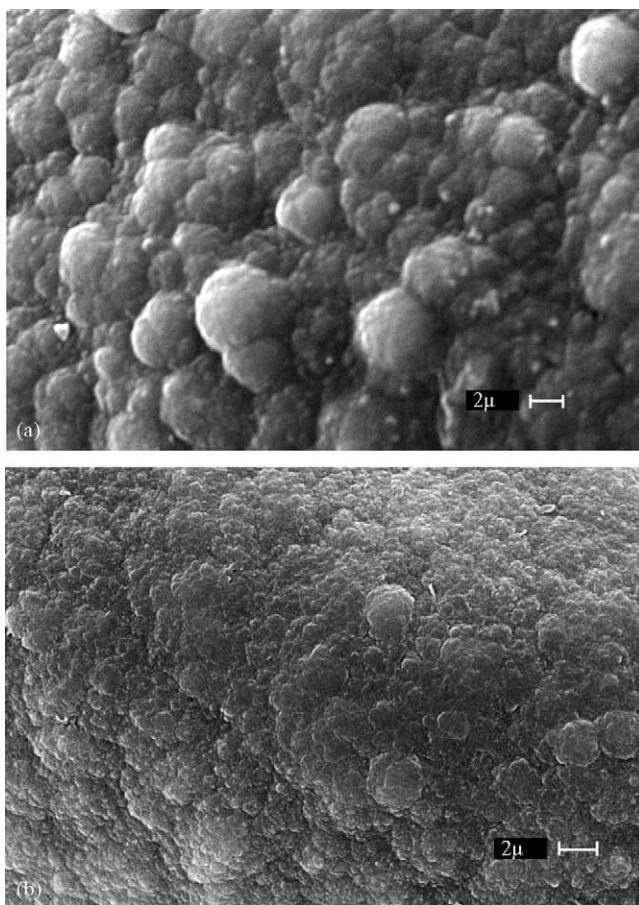


Fig. 3. SEM images of polypyrrole on different substrates: (a) platinum mesh and (b) stainless steel mesh.

over-oxidized forms of polypyrrole are less conductive. With a Pt substrate electrode, the effective polymer deposition occurred only when the applied potential was more positive than +0.70 V (see Fig. 2b). Over-oxidation was observed when the applied potential was greater than +0.90 V.

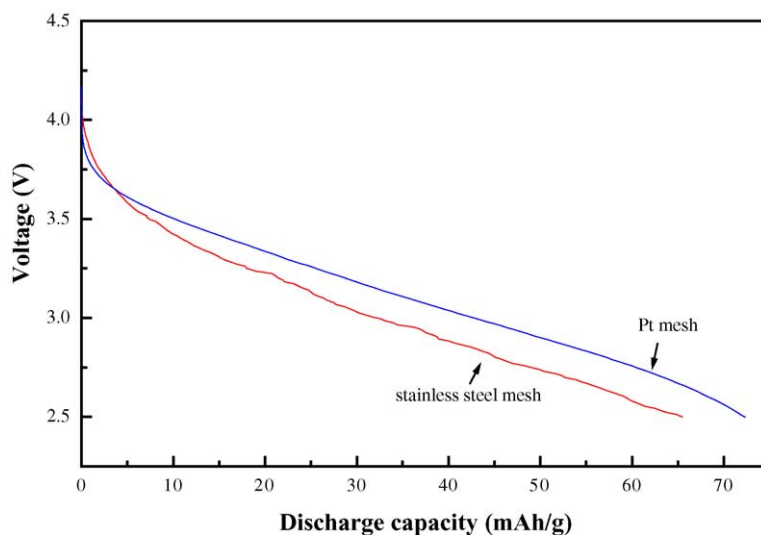


Fig. 4. Discharge curves of a Li/polypyrrole cell with different substrates.

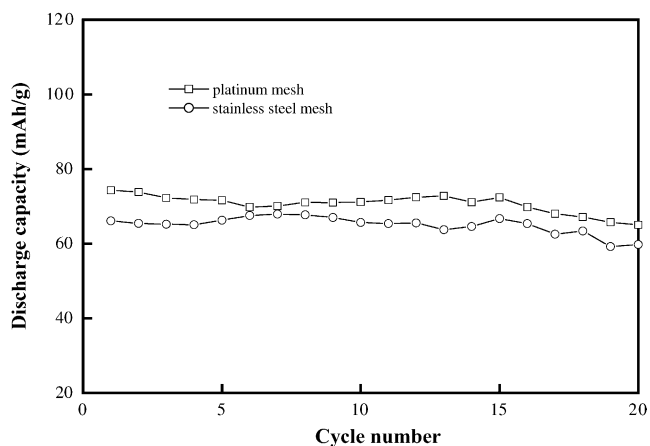


Fig. 5. Discharge capacities vs. cycle number for the cathode of polypyrrole coated on substrates. Discharge current density was  $0.1 \text{ mA cm}^{-2}$ .

Based on the above results, an applied potential of +0.75 V was selected for all subsequent experiments.

### 3.3. Morphology of polypyrrole films

SEM images of polypyrrole films deposited on the two different substrates were obtained (Fig. 3). A typical ‘cauliflower’ like nodular structure of electrochemically synthesized polypyrrole films is observed [18]. The morphology of the polypyrrole film deposited on the platinum mesh is coarse and more porous, while the film formed on the stainless steel mesh appears finer and dense.

### 3.4. Electrochemical performance

Polymerization of pyrrole (Py) produces the highly conductive and oxidized (doped) form of polypyrrole in which some electrons are removed from a delocalised  $\pi$ -system. The electro-neutrality of the oxidized polymer is retained by

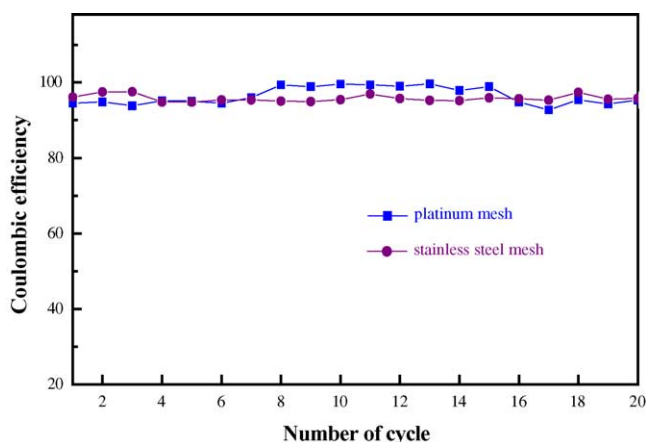
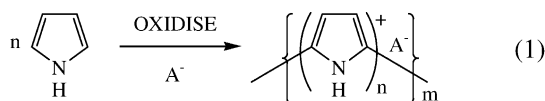


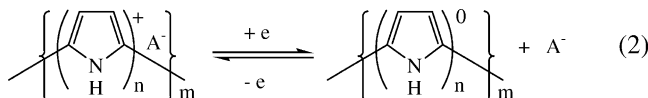
Fig. 6. Dependence of coulombic efficiency on cycle number for cells with polypyrrole coated platinum mesh or polypyrrole coated stainless steel mesh.

the incorporation of an adequate amount of anions from the electrolyte into the bulk of PPy according to:



$n$  indicates degree of doping (usually 2–4) [19],  $m$  determines molecular weight. Protons are also produced during polymerization from the breaking of C–H bonds [20].

During discharge, the polymer is reduced (undoped) to its neutral state by releasing the anion:



When charged again, anions migrate back into the polymer.

Fig. 4 shows the discharge curves (10th cycle) of the cells with polypyrrole on different substrates at the current density of  $0.1 \text{ mA cm}^{-2}$ . When discharged, the potential of the elec-

trode quickly dropped to 3.5 V and then followed an approximately half parabolic curve until the cut-off voltage of 2.5 V was reached. The discharge curve of the cell with polypyrrole on platinum mesh is slightly higher than the cell using stainless steel mesh as the substrate. But no obvious discharge plateaus were observed for both cells.

Fig. 5 shows discharge capacities versus the cycle number for the cells fabricated with polypyrrole on the two different substrates. The results indicate that the cell with polypyrrole on platinum mesh has slightly higher discharge capacities than that of the cell with stainless steel mesh as substrate. This may be because the conductivity of the platinum mesh is higher than that of stainless steel mesh. The higher capacity observed for the cell with polypyrrole on platinum mesh may also be due to the morphology of the film. The polypyrrole film using platinum mesh as substrate shows a more porous structure (see Fig. 3). The surface area should be larger, so the reactivity of active material with electrolyte was higher compared with the cell with polypyrrole on stainless steel mesh.

The coulombic efficiencies of the cells with polypyrrole on the two substrates are all high, above 95% (see Fig. 6), as given by the ratio of the discharge capacity to the charge capacity. The coulombic efficiency of the cells using platinum mesh or stainless steel mesh as substrates are similar.

Electrochemical impedance spectroscopy (EIS) was performed on electrodes of polypyrrole coated platinum mesh and stainless steel mesh. Fig. 7 shows the impedance results obtained for the cells of polypyrrole on the two different substrates. At high frequencies, the impedance response exhibits a semicircular loop. The diameter of this semicircle gives a charge-transfer resistance that is a measure of the charge-transfer kinetics. The results indicate that the charge-transfer resistance of the cell using the platinum mesh as electrode substrate is lower than the film on the stainless steel mesh.

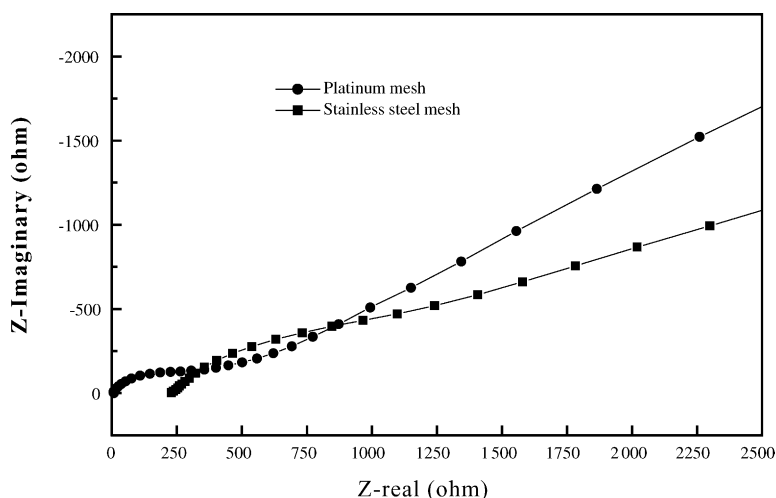


Fig. 7. Impedance plots for the polypyrrole films on the platinum mesh and stainless steel mesh in 0.5 M LiClO<sub>4</sub>/propylene carbonate.



#### 4. Conclusion

The light and inexpensive stainless steel mesh has been tested as an electrode substrate for a Li/polypyrrole rechargeable battery. The stainless steel mesh is thin, lightweight, flexible, has good conductivity, and can be formed into various configurations. Although the electrochemical performance of the cell using polypyrrole coated stainless steel mesh is slightly lower than that of the polypyrrole coated platinum mesh, stainless steel mesh is much cheaper and is a very promising substrate material for manufacturing polymer batteries.

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