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A cytocompatible robust hybrid conducting polymer hydrogel for use in a magnesium battery

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A cytocompatible robust hybrid conducting polymer hydrogel for use in a magnesium battery

Abstract

A cytocompatible robust hybrid conducting polymer hydrogel, polypyrrole/poly(3,4-ethylenedioxythiophene) is developed. This hydrogel is suitable for electrode-cellular applications. It demonstrates a high battery performance when coupled with a bioresorbable Mg alloy in phosphate-buffered saline. A combination of suitable mechanical and electrochemical properties makes this hydrogel a promising material for bionic applications.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Yu, C., Wang, C., Liu, X., Jia, X., Naficy, S., Shu, K., Forsyth, M. & Wallace, G. G. (2016). A cytocompatible robust hybrid conducting polymer hydrogel for use in a magnesium battery. *Advanced Materials*, 28 (42), 9349-9355.

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DOI:

Article type: Communication

A cytocompatible robust hybrid conducting polymer hydrogel for use in a magnesium battery*Changchun Yu, Caiyun Wang*, Xiao Liu, Xiaoteng Jia, Sina Naficy, Kewei Shu, Maria Forsyth, Gordon G. Wallace**

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Keywords: Conducting polymers; Hydrogels; Magnesium battery; Cytocompatibility; Electrode-cellular application.

The advent of bionic materials that utilise electrical stimulation to promote tissue regeneration has highlighted the need for integrated energy storage systems.^[1] A Mg-air battery is a promising candidate due to the high energy density and high discharge voltage attainable as well as the bioresorbability of Mg or Mg alloys.^[2] Mg^{2+} produced during battery discharge is the fourth most abundant cation in the human body and can promote human tissue growth.^[3]

A high performance Mg air battery requires an efficient cathode with a highly porous structure facilitating the O_2 reduction reaction (ORR).^[4] Conducting polymers (CPs) possess

the merits of high conductivity, biocompatibility and are catalytic towards the ORR. The use of CPs in biocompatible Mg batteries with a biological electrolyte has been demonstrated previously.^[5]

Hydrogels are extremely suitable for a variety of bio-applications.^[6] Conducting hydrogels used in tissue engineering typically consist of nonconductive scaffolds with a conducting polymer coating.^[7] These hydrogels possess excellent mechanical properties, however, they suffer from low electroactivity and hence are not suitable for application in batteries. Conducting polymer-based hydrogels (CPHs) wherein electronic conductivity is introduced into the structure with little compromise of the physical properties are interesting. The 3D interconnected porous structure with gel like mechanical properties make them highly suitable for tissue engineering,^[8] such as poly(3-thiopheneacetic acid) hydrogel.^[9]

CPHs for use energy storage applications are commonly in the form of composites with graphene or carbon nanotubes.^[5c, 10] Ghosh *et al.* have demonstrated a polypyrrole/poly(3,4-ethylenedioxythiophene, PEDOT) hydrogel as a supercapacitor electrode,^[11] however, they used the pre-formed PEDOT film (about 2/3 of the contained water was evaporated) for ionic cross-linking forming the hydrogel, since PEDOT dispersion can easily disintegrate upon the direct contact with high concentration Mg^{2+} solution and difficult to form a bulk hydrogel.^[12] There are significant limitations in controlling the structure due to the additional processes introduced including film forming, drying and re-swollen. Polyaniline hydrogels^[13] or polypyrrole hydrogels^[14] prepared by chemical polymerization have demonstrated a high conductivity for application in energy storage, but they require a long purification time to remove any excess reactants or by-products. Furthermore, little information is available on the mechanical properties of these CPHs, nor their application in tissue engineering.

Herein we demonstrated a cytocompatible PPy/PEDOT hydrogel for use in a Mg battery. Polypyrrole is electrochemically deposited onto the PEDOT hydrogel obtained by a two-step

cross-linking process. This robust hybrid hydrogel combines offers good electrochemical properties, in addition to being cytocompatible.

In the PEDOT:PSS compound, PSS is in excess with respect to the positively charged PEDOT chain.^[15] Excessive negative charge of the PEDOT:PSS complex can be ionically crosslinked in solution by multivalent cations. The cation of Mg^{2+} can electrostatically interact with PSS as an ionic crosslinker (**Figure 1A**) in this work. The procedure to fabricate a PEDOT hydrogel includes a two-step ionic crosslinking process. An additional electropolymerization process is applied for PPy/PEDOT hydrogel (Figure 1B). The addition of low concentration $\text{Mg}(\text{NO}_3)_2$ was sufficient to convert the viscous PEDOT:PSS dispersion into a monolithic gel, capable of maintaining its structure under gravity (Figure 1C). The PEDOT film that was partially crosslinked with Mg^{2+} can maintain its integrity when contacting with 1 M Mg^{2+} solution, in contrast to the disintegration of the pure PEDOT film (Figure S1, Supporting Information). It has been reported that aqueous PEDOT:PSS film are easily disintegrated in excess Mg^{2+} solutions rather than gelation occurring.^[11-12] The initial crosslinking step allows Mg^{2+} to evenly distribute throughout the PEDOT:PSS dispersion and slightly crosslink it. This process is essential to maintain a uniform hydrogel avoiding local gelation when contact with high concentration Mg^{2+} solution. The use of a higher concentration of Mg^{2+} in the second step is to increase the degree of crosslinking and thus improve the overall strength of the hydrogel.

The PEDOT hydrogel changed colour from dark blue (Figure 1D, left) to black (Figure 1D, right) after the incorporation with PPy. A higher deposition current was produced during the PPy growth on PEDOT hydrogel, compared to that with stainless steel substrate at the same applied potential (Figure S2, Supporting Information). It can be ascribed to the increased surface area ascribed to the hydrogel's 3D porous structure as well as its good compatibility with electrolyte. The PPy/PEDOT hydrogel materials were mechanically robust, and still

retained the shape without any volume loss after removing the mould. Therefore, it is possible to fabricate a PPy/PEDOT hydrogel with any desired shape or size using this method. This free-standing hydrogel is robust, and can be lifted by a pair of tweezers. In contrast, PEDOT hydrogels were collapsed under their own weight (Figure 1D). Both hydrogels displayed a sharp mass loss between 50°C and 100°C in the TGA measurement (Figure 1E), which is associated with water contained in the structure. The water content was estimated to be 97.5% for PPy/PEDOT hydrogel, and 98.2% for PEDOT hydrogel.

The PEDOT gel had properties resembling a highly concentrated polymer solution with a plateau region of storage modulus G' around 2.5–3.2 kPa (Figure 1F), demonstrating a compression fracture strength of 1.6 kPa and a Young's modulus of 0.9 kPa (Figure 1G). In contrast, the PPy/PEDOT hydrogel exhibited a robust gel-like behaviour with G' remaining almost constant around 13.5–19.3 kPa, higher than that (~3 kPa) of poly(*N*-isopropylacrylamide)/PPy hydrogel.^[14c] It also exhibited a much higher compression fracture strength and a Young's modulus respectively 12.4 kPa and 7 kPa. Such enhancement is attributed to the incorporation of the stiffer PPy network into the PEDOT hydrogel matrix providing additional reinforcement and mechanical support. The modulus can be further improved to ~12 kPa and ~32 kPa when the charge consumed during PPy growth was increased by 150% and 200% (Figure S3, Supporting Information). This modulus range (7–32 kPa) matches that of adipose (2 kPa), neurons (1–10 kPa), and skeletal muscle (~30 kPa) tissue,^[16] thus making these PPy/PEDOT hydrogels candidates for tissue regeneration.

Freeze-drying is a pore-protecting drying method, and is widely used to process hydrogels to characterise the porous structure.^[17] Both PEDOT (**Figure 2A**) and PPy/PEDOT hydrogel (Figure 2B) displayed a typical 3D interconnected porous structure. In general, PPy/PEDOT hydrogel matrix had a more coarse network (Figure 2E), compared to that of PEDOT (Figure 2D). This coarse surface was composed of granules at higher magnification, clearly

.. demonstrating the existence of PPy. PPy on the stainless steel mesh showed a granular surface morphology (Figure 2C, 2F). Both PEDOT and PPy/PEDOT hydrogels demonstrated a similar cross-sectional view being a typical hydrogel structure (Figure 2G, 2H). The elements contained in these hydrogels were examined using energy-dispersive X-ray spectroscopy (EDS) associated with SEM (Figure 2I-N). Elements, C, S and O, are detected in all these three samples. Mg is observed in the PEDOT and PPy/PEDOT hydrogel, which is from the crosslinking agent used, $\text{Mg}(\text{NO}_3)_2$. The element N is from pyrrole ring. The presence of N in the PPy/PEDOT hydrogel proves the successful deposition of PPy onto PEDOT hydrogel.

The PEDOT hydrogel alone displayed a negligible current response when scanned over the range of -0.7 V to 0.6 V at a scan rate of 20 mV/s (**Figure 3A**), whereas with a PPy coating, both the anodic and cathodic current improved significantly. Cyclic voltammograms (CVs) obtained from electrode with PPy alone had lower current densities for both oxidation and reduction compared with the PPy/PEDOT composite. Given the equivalent amount of PPy was electrodeposited in both cases as well as the negligible response from PEDOT alone. The significantly higher current response from PPy/PEDOT hydrogel can be attributed to its porous structure facilitating fast electron and ion transport.^[18] Not surprisingly, the current response increased with the increased amount of PPy deposited (Figure S4, Supporting Information). It is also noted that the oxidation peak shifted positively and the reduction peak shifted negatively with increasing scan rate (Figure 3B), and this is attributed to the electrode resistance.

The open circuit potential of the reduced PPy/PEDOT hydrogel (-0.8 V, 1800s) increased immediately after the bias potential was removed (Figure 3C) in an O_2 -rich or N_2 -saturated PBS electrolyte. A potential of -0.04 or -0.30 V were recorded at 400s, respectively. A higher

potential increase in the O₂-rich electrolyte suggests that the reduced hydrogel can be readily re-oxidized by O₂.

The PPy/PEDOT hydrogel, PPy or PEDOT hydrogel displayed a bulk resistance of 15 Ω , 35 Ω and 10 Ω in PBS electrolyte, respectively (Figure 3D). The lowest bulk resistance of the PEDOT hydrogel arises from its superior electrical properties compared with PPy.^[19] The PPy/PEDOT hydrogel displayed a smaller resistance in the medium-high frequency region compared to pure PPy, suggesting its fast electrochemical kinetics.^[20] Neural cell communication commonly occurs between 300 Hz and 1 kHz.^[21] PPy/PEDOT showed its excellent transportation behaviour as evidenced by a low impedance of 10 Ω at 1 kHz, lower than 37 Ω for PPy (Figure 3D, inset) and the previously reported K Ω level for the PEDOT hydrogel.^[22] The low resistance is beneficial to recording high quality signals when used in vivo.

A Mg battery composed of PPy/PEDOT hydrogel or PPy was discharged for 6h at various discharge current densities (Figure 3E). PPy/PEDOT hydrogel displayed a discharge plateau of 1.35, 1.20, 1.10, 0.93 and 0.45V, compared to 1.42, 1.26, 0.75, 0.55 and 0.27 V for PPy at 20, 50, 100, 200 and 500 $\mu\text{A}/\text{cm}^2$, respectively. It can be seen clearly that at a discharge current above 100 $\mu\text{A}/\text{cm}^2$, a PPy/PEDOT hydrogel battery displayed a higher discharge voltage indicating its better ORR catalytic ability at these discharge rates.^[23] This may be explained by the fact that the porous conductive framework facilitates rapid electron transfer and shortens ion diffusion distances leading to better performance at higher current densities.

The Mg battery with a PPy/PEDOT cathode could provide a stable voltage of 0.7 V for about 160 h at a current density of 200 $\mu\text{A}/\text{cm}^2$, delivering a capacity of 32 mAh cm^{-2} and an energy density of 22 mWh cm^{-2} (Figure 3F). This performance is superior to the 60 h for PPy with a capacity of 12 mAh cm^{-2} and energy density of 10 mWh cm^{-2} . The power to drive the implantable medical devices (IMDs) generally falls in the level of μW to mW,^[24] and

therefore the battery containing a PPy/PEDOT cathode is expected to power IMDs such as a pacemaker, cardiac defibrillator or a neurological stimulator.

The cytotoxicity of PPy/PEDOT hydrogel was evaluated using adipose-derived stem cells (hADSCs). As shown in the live/dead fluorescence staining (**Figure 4A**), hADSCs were well spread and reached high confluence at 72 h after seeding, which indicates low cytotoxicity of the substrate. In agreement with the fluorescence image, the SEM images exhibited a flat, well spread cell morphology, with minor filopodia attached tightly to the PPy/PEDOT hydrogel. These cells were forming bridges over the highly porous substrate (Figure 4B, 4C). The total cell metabolic activity, characteristic of cell proliferation, increased significantly during the first 2 weeks, then stabilised (Figure 4C). These results demonstrate that this conductive PPy/PEDOT hydrogel provides a compatible substrate for hADSCs. Given the conductivity and electroactivity this organic conducting polymer based hydrogel could also serve as a conduit for electrostimulation to provide benefits as described previously.^[25]

In summary, a robust hybrid conducting polymer hydrogel (PPy/PEDOT) has been developed for a Mg biobattery. By introducing a two-step crosslinking method, it is feasible to fabricate any desirable size and shape hydrogel. The incorporation of PPy reinforces the hydrogel scaffold, demonstrating the mechanical properties suitable for use as a bio-interface. The battery assembled with this hybrid hydrogel possess high capacity, high rate and high energy density due to its three dimensional porous structure. It can be anticipated that the energy generated from this type of biobattery may be directly used to modulate cellular activities cultured on the hydrogel without need of an external power supply.

Experiment Section

Materials: Pyrrole, toluene-4-sulfonic (sodium salt) (*p*TS), phosphate buffered saline (PBS) tablet were obtained from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene)

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polystyrene sulfonate (PEDOT: PSS) pellets were from Agfa Company. PBS solution was prepared by dissolving a PBS tablet in 200 mL deionized water (pH 7.4). Gibco Dulbecco's Modified Eagle's Medium (DMEM), Fetal bovine serum (FBS), penicillin-streptomycin, calcein and propidium iodide (PI) were obtained from Life technologies (Australia). Commercial human adipose-derived stem cells (hADSCs) obtained from Lonza company were cultured in DMEM supplemented with 10% (v/v) FBS in a humidified incubator at 37 °C with 5 % CO₂ atmosphere.

PPy/PEDOT hydrogel Fabrication: A 1.5 wt% PEDOT:PSS dispersion (3 ml) was mixed with 0.25 M Mg(NO₃)₂ (360 µL). This partial ionic crosslinking process lasted 24 h in a cuboid conductive template, followed by immersion in 1 M Mg(NO₃)₂ overnight for additional crosslinking. Then it was immersed in 0.1 M freshly distilled pyrrole and 0.1 M *p*TS solution for 2 h at 4 °C prior to commencing the electropolymerization (0.7 V vs Ag/AgCl). A similar procedure was followed to fabricate PPy/PEDOT hydrogel on stainless steel mesh for electrochemical tests and cell work. The uniformly mixed 1.5% PEDOT:PSS and 0.25 M Mg(NO₃)₂ solution (60 µL) was cast on a UV-ozone-treated stainless steel mesh (1 x 1 cm²). The samples were kept in hood for 20 min for gelation before being immersed in 1 M Mg (NO₃)₂ for 2 h. The applied charge for PPy electropolymerization (0.7 V vs Ag/AgCl) was 1 C. Polypyrrole (PPy) on stainless steel mesh was also prepared as a control sample.

Cell work: PPy/PEDOT hydrogels were treated by soaking in sterile PBS supplemented with 500 U/ ml Penicillin-Streptomycin for 20 h. The hydrogels were placed into six-well polystyrene cell culture plates and soaked overnight with culture medium, followed by rinsing with PBS twice. Adipose-derived stem cells (hADSCs) were seeded on the samples at the density of 3×10⁴ cells/cm², and cultured in DMEM media supplemented with 10% FBS for 72 h. Then cells were visualized using Live/Dead (calcein-AM/PI) staining with 2 µM Calcein AM and 4 µM PI in PBS. Images were obtained using a ZEISS Axio Imager

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microscope (Carl Zeiss). For SEM imaging, the hADSCs were fixed in 3.7% paraformaldehyde for 1 h at room temperature, followed by a frozen process in liquid nitrogen and a freeze drying process.

For the proliferation study, cells were seeded at 10^4 cells/cm² in a 24 well plate. Cell viability and proliferation ability were measured by PrestoBlue (Life technology). Specifically, at day 1, 3, 7, 14 and 21, cells were incubated in 10% Prestoblue (in culture media) for 1h. Fluorescence was measured by plate reader with a 544 nm excitation filter and a 590 nm emission filter.

Characterisation: The surface morphology or cross-sectional view of PPy, freeze-dried hydrogels of PEDOT or PPy/PEDOT was investigated by field emission scanning electron microscopy (JEOL JSM-7500FA). The thermal properties were recorded with a thermogravimeter (Q500 TGA analyzer) at a heating rate of 10°C/min. Compressive stress-strain measurements were performed on the equilibrated hydrogels (10×10×6 mm³) using a Shimadzu EZ-L universal mechanical tester at a crosshead speed of 1 mm/min. The Young's modulus was calculated using the slope of the stress-strain curve from 0 to 0.05 strain. Rheological experiments were performed on a TA AR-G2 rheometer with a parallel plates configuration (12 mm diameter) at a constant strain (0.1 %) and a constant normal force (0.1 N) while frequency was swept from 10^{-2} sec⁻¹ – 10 sec⁻¹.

Cyclic voltammetry tests were performed with an electrochemical workstation (CHI 650D). Impedance spectra were measured using a Gamry EIS 3000 system over the frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 10 mV at open-circuit potential. Batteries were assembled using a PPy-PEDOT hydrogel or a PPy cathode (1×1 cm²) coupled with a Mg alloy anode (1×1 cm²) in a one-component cell containing 10 mL PBS. The discharge test was carried out using a battery-testing device (Neware Electronic Co.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Funding from the Australian Research Council Centre of Excellence Scheme (CE 140100012) is gratefully acknowledged. C. Y. acknowledges the support of CSC scholarship from the Ministry of Education of P.R. China. G.G.W. is grateful to the ARC for support under the Australian Laureate Fellowship scheme (FL110100196). The authors would like to thank Australian National Fabrication Facility-Materials node (ANFF) and UOW Electron Microscopy Centre for equipment use.

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Figure 1 (A) Schematic procedures to fabricate PEDOT hydrogel and PPy/PEDOT hydrogel; (B) Crosslinking process of PEDOT:PSS hydrogel; (C) Digital images of freshly mixed 1.5% PEDOT and 0.25 M $Mg(NO_3)_2$ solution (left) and after the gelation (right); (D) Digital images of PEDOT hydrogel (left) and PPy/PEDOT hydrogel (right) after the template removal, inset shows the robust PPy/PEDOT hydrogel can be lifted by a tweezer; (E-G) TGA (E), rheological behaviours (F) and compressive stress-strain curves (G) of PPy/PEDOT hydrogel and PEDOT hydrogel.

Figure 2 Surface morphology of PEDOT hydrogel (A, D), PPy/PEDOT hydrogel (B, E), and PPy on a stainless steel mesh (C, F) (inset E, scale bar 100 nm); Cross-sectional images of PEDOT hydrogel (G) and PPy/PEDOT hydrogel (H); SEM images and the corresponding EDX spectra of PPy (I, L), PEDOT Hydrogel (J, M) and PPy/PEDOT Hydrogel (K, N).

Figure 3 A) Cyclic voltammograms of PPy/PEDOT hydrogel, PPy or PEDOT hydrogel in PBS at a scan rate of 20 mV s^{-1} ; B) Cyclic voltammograms of PPy/PEDOT hydrogel at different scan rates in PBS; C) Potential response of PPy/PEDOT hydrogel electrode in O_2 or N_2 saturated PBS solution after the bias potential (-0.8 V vs Ag/AgCl) was removed; D) Nyquist plot of a PEDOT hydrogel, PPy or PPy/PEDOT hydrogel in PBS (insets: left, expanded plot; right, Z vs. frequency); E) Discharge curves of a Mg battery with a PPy/PEDOT hydrogel or a PPy cathode in PBS at different discharge current densities (6h duration for each stage); F) Discharge curves of a Mg battery with PPy/PEDOT hydrogel or PPy cathode at $200 \mu\text{A cm}^{-2}$ in PBS.

Figure 4 A) Live/Dead cell viability staining (green, live cells; red, dead cells); B, C) SEM images of cell on PPy/PEDOT hydrogels; D) Growth curve of hADSCs on PPy/PEDOT hydrogel at day 1, 3, 7, 14, 21.

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A cytocompatible robust hybrid conducting polymers hydrogel, polypyrrole/poly(3,4-ethylenedioxythiophene) electrode is developed. This hydrogel is suitable for electrode-cellular application. It demonstrates a high battery performance when coupled with a bioresorbable Mg alloy in phosphate-buffered saline. A combination of suitable mechanical and electrochemical properties makes this hydrogel a promising material for bionic applications.

Keyword: Batteries; Hydrogels; Bioelectronics.

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A cytocompatible robust hybrid conducting polymer hydrogel for use in a magnesium battery