Hybrid Materials Polypyrrole-heteropolytungstate Electrosynthesis of Electrodes for Secondary Batteries

S.A.CHENG¹, T.F.OTERO

Laboratorio de Electroquímica, Departamento de Ciencia y Tecnología de Polímeros Facultad de Químicas, Universidad del País Vasco, P.O.Box 1072, 20018 San Sebastián, Spain

¹Present address: Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Polypyrroles doped with heteropolytungstate anion $[PW_{12}O_{40}]^{3-}$ was electrogenerated from acetonitrile solutions. It is found that the productivity of the consumed charge to produce the hybrids always keeps at high constant value of about $1.9 \times 10^{-3} \text{ mg mC}^{-1}$, whatever the studied conditions including different potentials, different concentrations of pyrrole, different concentrations of $PW_{12}O_{40}^{3-}$ or different temperatures. The hybrid material coats the electrode as a compact, adherent, conducting and dark-blue film. The specific charges of the materials initially increase as the polymer weight increases keeping a constant value for greater weight than 0.15 mg cm^{-2} . Consecutive charge-discharge promotes a fast initial loss of material by solubility, the specific charge of the insoluble part increases until 90 mA h g^{-1} . Both evolution of the cyclic voltammograms and UV-vis spectroscopies indicate the presence of macroanion in solution after cycling.

Key words: polypyrrole, heteropolytungstate, cyclic voltammetry, UV-vis spectroscopy

Materiales híbridos polipirrol-heteropolitwolframato electrosíntesis de electrodos para baterías secundarias

Los polipirroles dopados con anión heteropolitwolframato $[PW_{12}O_{40}]^{3-}$ (materiales híbridos) han sido electrogenerados desde disoluciones de acetonitrilo. Se ha visto que la productividad de la carga consumida para producir los híbridos siempre se mantiene a valores constantes elevados alrededor de $1.9 \times 10^{-3} \text{ mg mC}^{-1}$, cualquiera que sea la condición estudiada de síntesis: diferentes potenciales, diferentes concentraciones de pirrol, diferentes concentraciones de $PW_{12}O_{40}^{3-}$ o diferentes temperaturas. El material híbrido recubre el electrodo en forma de film azul marino, compacto, adherente y conductor. Las cargas específicas almacenadas en los materiales inicialmente aumentan a medida que el peso del polímero aumenta, manteniendo un valor constante a partir de pesos mayores que 0.15 mg cm^{-2} . La voltamperometría cíclica y la espectroscopía UV-vis indican la presencia de un intercambio de iones entre el macroión del film y el ClO_4^{-1} de la solución durante los procesos de oxidación-reducción. Las respuestas electroquímicas de los híbridos están fuertemente afectadas por el contenido del macroión.

Palabras clave: polipirrol, heteropolitwolframato, voltamperometría cíclica, espectroscopía UV-vis.

1. INTRODUCTION

Heterocyclic conducting polymers such as polypyrrole, polyaniline or polythiophene with immobilized polyoxometalates have been attracting much interest in electrocatalysis and in electrochemistry. A rich literature exists on polypyrrole films doped with Keggin-type polyoxometalates. Electrocatalytic (1-5) hotoelectrochemical (6-7) and electrochemical (8-9) properties of these materials have previously been reported. However, polyoxometalate anions in films can provide a secondary mechanism to store charge due to the fact that they are capable of reversible redox reactions interchanging electrons without any change in the original structure. These hybrid materials should have the higher specific storage charge when considered for application in the secondary batteries. The aim of this paper was to determine how the synthesis conditions influence both production and properties of polypyrrole films doped with heteropolytungstate anion $[PW_{12}O_{40}]^{3-}$ electrogenerated from acetonitrile.

2. EXPERIMENTAL PROCEDURE

The heteropolyacid $H_3Pw_{12}O_{40}$ was supplied by Fluka and used as received. Pyrrole (Jansen) was distilled at 59°C under

vacuum (50 torr) and stored at low temperature in dark before use. All other chemicals were reagent grade and were used as received. Hybrid materials of polypyrrole doped with heteropolytungstate anion $[PW_{12}O_{40}]^{3-}$ were electrogenerated from acetonitrile solutions containing pyrrole, heteroma-croion and 2% of water at anodic potentials greater than 800 mV vs Ag/AgCl. The empirical kinetics were obtained by ex-situ microgravimetry from different concentrations of pyrrole (0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.4 M), different concentrations of heteropolytungstate acid (0.001 M, 0.0025 M, 0.005 M, 0.01 M, 0.02 M), different temperatures (-5°C , 5°C , 22°C , 35°C). The hybrid films for UV-vis investigation were prepared by electrochemical oxidation in 0.1 M Py +0.005 M $H_3PW_{12}O_{40}$ +2%(v/v) H_2O acetonitrile solutions by polarizing at 500 mV for 60s and following a step up to 1200 mV for 135 mC. A platinum sheet with a surface area of 1 cm^2 was as working electrode, a stainless steel having 3 cm^2 of surface area was the counter electrode. All the electrode potentials cited in this paper are referred to the Ag/AgCl electrode. All the experiments were performed under nitrogen atmosphere and at room temperature. After generation or after cycling, the coated electrode was rinsed with acetone and weighed after

dried in hot air. The film weight was evaluated by difference between the uncoated working electrode and the coated electrode or between the coated electrode before cycling and the coated electrode after cycling, using a 4504 MP8 Sartorius ultramicrobalance (10^{-7} g precision).

A M273 PAR potentiostat-galvanostat connected to a PS-5 IBM microcomputer and driven by means of M273 software from EG&G was used for both electrogeneration and checking of polymer film.

UV-vis absorption spectra were performed on PU8700 Series UV/VIS Spectrophotometers.

3. RESULTS AND DISCUSSION

3.1. Productivity of the polymerization charge

By integration of every chronoamperogram, the electrical charge consumed during polymerization was obtained. The results show a good linear relationship between polymer weight and consumed electrical charge under any of the studied variables of synthesis: different potential, different concentration of pyrrole, different concentration of $PW_{12}O_{40}^{3-}$, or different temperature. The ratio between polymer weights and the concomitant consumed polymerization charge gives the productivity of the charge consumed during synthesis. A constant productivity (around 1.9×10^{-3} mg mC^{-1}) independent of the studied potential was obtained. This productivity is about 4 - 10 times the productivity attained when basic polypyrroles or polypyrrole-polyelectrolyte blends were electrogenerated (4,10-11). There, the productivity of the charge decreases generally as more anodic potentials of synthesis were used due to the presence of side reactions as solvent or electrolyte oxidation (11-14). The constant productivity found in this system seems to point to an uniform electrogeneration mechanism of the hybrid material inside the range of the studied variables. Under those conditions we can assume that the electrogeneration of the hybrid material is the only significant reaction. If parallel reactions consuming charge without any production of the material were present they should have the same dependence on the studied variable that the one observed for the polymerization rate.

3.2. Specific charges of the formed hybrid materials

Every formed material was checked by cyclic voltammetry in a 0.1 M $LiClO_4$ acetonitrile solution. By integration of the each control voltammogram the stored charge of each formed polymer is obtained. Specific charge the electrical charge stored per mg of electrogenerated material is obtained by following equation.

$$\text{Specific charge (mA h g}^{-1}\text{)} = Q_{ox} / (3.6 \cdot W)$$

Here, the Q_{ox} represents the charge stored in a film expressed in mC and the W the film weight expressed in mg. Fig.1 shows the plot of the specific charges vs. the weights of formed polymers at different potentials, different concentrations of pyrrole, different concentrations of $PW_{12}O_{40}^{3-}$ and different temperatures. From Fig.1 we can observe that the specific charges initially increase as the polymer weight increases and then keeps almost a constant value when the polymer weight is up to about 0.15 mg cm^{-2} . A partial dissolution of the material occurs during consecutive cycling. Specific charge in the insoluble part increases until 90 mA h mg^{-1} .

Fig.1 Evolution of the composite film storage charge with polymer weight at all studied conditions: different potentials, different concentrations of Py, different concentrations of heteropolyanion and different temperatures.

Fig.2 Consecutive voltammograms of hybrid material in 0.1 M $LiClO_4$ acetonitrile solution. Scan rate: 20 mV s^{-1} .

3.3. Voltammetric behaviour

When a just formed film of the hybrid material was cycled in 0.1M $LiClO_4$ acetonitrile solution, between -800 mV and 400 mV (vs. Ag/AgCl), the consecutive 20 initial voltammograms show a continuous evolution (Fig.2). The initial voltammogram shows a shoulder and a maximum in both branches (A and B on the anodic one and C and D on the cathodic) in the potential region ranging between -350 mV and 100 mV. At more anodic potentials a capacitive region exists.

On the consecutive voltammograms those maxima and shoulders show decreasing current densities. At the same time a new anodic maximum (E), and its concomitant cathodic maximum (F) are formed at more cathodic potentials, -350 mV and -580 mV, respectively, showing increasing current densities on the consecutive voltammograms.

None of those new maxima, E and F, are formed if the cathodic potential limit does not surpass -600 mV, meanwhile a similar continuous drop is observed on the two initial maxima. The formation and growth of maxima E and F is still observed if we cycle the film between -800 and -200 mV.

The just formed film of the hybrid material weighed about 0.2560 mg and taking into account the charge stored in the first anodic voltammogram 16.75 mC a low specific charge of 17.5 mA h g⁻¹ was obtained. Nevertheless, at the end of the first voltammogram, the weight of the dried material was 0.0529 mg, being the concomitant specific charge of 88 mA h g⁻¹. Taking into account the great decrease on the material lost, films cycled during different consecutive voltammograms were weighted, once dried. Weights and specific charge evaluations are shown on figure 3.

The most surprising aspect of those results is the great diminution of the material weight. Considering the low solubility of the polymer, the observed variation should be attributed to a lost of the macroanion from the film. In order to check this hypothesis, the cell solution was analysed by UV-vis spectroscopy.

3.4. Changes on the solution composition

Working with a different film and a fresh solution every time, the background solution was analysed by UV-vis spectroscopy. Those solutions show (figure 4) an important concentration of the macroanion.

A just electrogenerated film, once dried and weighed, was put in a solution of acetonitrile with 0.1 M LiClO₄ for several hours. After this time the presence of macroions in the solution was not detected by UV-vis, and the weight of the film, once dried, was not changed, showing that in the previous experiments the solution of the macroanion and the weight loss of the material are mainly related to the oxidation reduction processes occurring during the potential cycling.

4. CONCLUSIONS

Hybrid materials of polypyrrole doped with heteropolytungstate anion [PW₁₂O₄₀]³⁻ were electrogenerated from acetonitrile solutions containing pyrrole, heteromacroion and 2% of water at anodic potentials greater than 800 mV vs Ag/AgCl. The productivity of the hybrid material always keeps at high constant value of about 1.9 × 10⁻³ mg mC⁻¹, whatever the studied conditions. The specific charges of the materials initially increase as the increase of the polymer weight and then keep an almost constant value when the polymer weight is up to about 0.15 mg cm⁻². The hybrid films show a flat morphology. The cyclic voltammograms and UV-vis spectroscopies indicate the present of macroion in solution after cycling. Taking into account the great decrease on the material mass, the specific charge of 90 mA h g⁻¹ of the insoluble hybrid materials was obtained

ACKNOWLEDGMENTS

This work was supported by the Basque government.

REFERENCES

1. B.Keita, D.Bouaziz, L.Nadjo, A.Deronzier, "Surface functionalization with oxometallates entrapped in polymeric materials" *J.Electroanal.Chem.*, **279**,187-203(1990).
2. G.Bidan, E.M.Genies, M.Lapkowski, "Modification of polyaniline films with heteropolyanions: electrocatalytic reduction of oxygen and protons" *J. Chem.Soc.,Chem.Comm.*,533-535(1988)
3. B.Fabre, G.Bidan, "Electrocatalytic behaviour of an electrode coated with a nitrite-sensitive layer based upon an iron-substituted heteropolytungstate doped with poly(N-methylpyrrole)" *J.Chem.Soc., Faraday Trans.*, **93**, 591-601(1997).

Fig.3 Evolution of film weights and specific charges as the cycling number.

Fig.4 UV-vis spectra of the cycled solution (---), comparing with that of background solution containing 8 × 10⁻⁶ M H₃PW₁₂O₄₀ (—).

4. M.Lapkowsk, W.Turek, M.Barth, S.Lefrant, "Changes in catalytic properties of substituted heteropolyacids in conductive polymer matrix" *Synth.Met.*, **69**, 127-128(1995)
5. P.Wang, Y.Li, "Electrochemical and electrocatalytic properties of polypyrrole film doped with heteropolyanions" *J.Electroanal.Chem.*, **408**, 77-81(1996)
6. E.Papacostantinou, "Photocatalytic oxidation of organic compounds using heteropoly electrolytes of molybdenum and tungsten" *J.Chem.Soc.,Chem. Commun.*, 12-13(1982)
7. T.Ohtsuka, T.Wakabayashi, H.Einaga, "Optical characterization of polypyrrole-polytungstate anion composition films" *Synth.Met.*, **79**, 235-239 (1996)
8. H.Sung, H.So, W.K.Paik, "Polypyrrole doped with heteropolytungstate anions" *Electrochim. Acta*, **39**, 645-650(1994).
9. K.Cho, S.D.Chung, K.Ryu, Y.Kim, J.-H.Choy, H.Kim, "Electrochemical property of surface modified polypyrrole film with heteropolyanions" *Synth. Met.*, **69**, 481-482(1995).
10. T.F.Otero, C.Santamaria, "Dependence of polypyrrole production on potential" *Synth. Met.*, **51**, 313-319(1992).
11. T.F.Otero, J.Rodriguez, "Parallel kinetic studies of the electrogeneration of conducting polymers: mixed materials, composition and kinetic control" *Electrochim. Acta*, **39**, 245-253(1994).
12. T.F.Otero, C.Santamaria, "Kinetics of the polypyrrole electrogeneration from aqueous solution, An Ex situ microgravimetric study" *Electrochim. Acta*, **37**, 297-307(1992).
13. T.F.Otero, J.Rodriguez, "Polythiophene electrogeneration on a rotating disc electrode. The water content influence on polymerization and on the polymer properties" *J.Electroanal.Chem.*, **310**, 219-237(1991).
14. T.F.Otero, J.Rodriguez, E.Angulo, C.Santamaria, "Kinetics of polypyrrole and polythiophene electrogeneration followed by microgravimetry" *Synth. Met.*, **43**, 2831-2836(1991).