

Hybrid organic–inorganic nanocomposite materials for application in solid state electrochemical supercapacitors

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Abstract

Integration into a conducting polymer matrix to form a hybrid material is an effective way to harness the electrochemical activity of nanosized oxide clusters. By anchoring them into polyaniline, the reversible redox chemistry of the otherwise soluble polyoxo-metalate clusters can be combined with that of the conducting polymer and be put to work in energy storage applications. We present here preliminary results that show how the resulting hybrid polymer displays the combined activity of its organic and inorganic components to store and release charge in a solid state electrochemical capacitor device.

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1. Introduction

Polyoxometalates (POMs) have traditionally been the subject of study of molecular inorganic chemistry [1]. Their well-defined structure and their reversible multi-electron electrochemical reactions and photoelectrochemical properties make of them structural and functional models for nanometric oxide particles [1–3]; and it is precisely their molecular nature and good solubility that have prevented these systems to be used as functional materials, e.g., as electrodes for energy storage applications. On the other hand, conducting organic polymers have been extensively studied as promising novel materials, and the representative studies include reports on their possible use for rechargeable batteries [4–8] and electrochemical capacitors [9–13]. One of the frequent problems related to the application of conducting polymers is a relatively low capacity to store charge in such devices. The combination of conducting

polymers and electroactive molecular [14–18], cluster [19–21] or extended [22–30] inorganic species to form nanocomposite hybrid materials represents an opportunity for the design of materials with improved properties (stability, charge propagation dynamics) and enhanced energy storage capabilities. Indeed, the anchoring of POMs within the network of conducting organic polymers such as polyaniline or polypyrrole leads to the fabrication of hybrid materials in which the inorganic clusters keep their integrity and activity [19–21] while benefiting from the conducting properties and polymeric nature of the hybrid (composite) structure [31,32]. Some of these hybrid materials have been studied in non-aqueous solvents as lithium-inserting electrodes for the potential use in lithium batteries [19,20]. However, under such conditions, the electroactivity of POM could not be harnessed for too many charging–discharging cycles. Furthermore, the electroactivity of these inorganic clusters integrated in a hybrid material is heavily dependent of the electrolyte used [7,14]. Thus, the use of aqueous acidic electrolytes, facilitates the counterion flux and promotes the concomitant protonation of the cluster upon reduction, leading

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to a quick and reversible redox chemistry. It should be noted that the POM clusters – the archetype of which is the Keggin type phosphomolybdic acid, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, shown in the inset of Fig. 1 – provide an ultimate degree of dispersion for an oxide phase since all 12 MO_6 moieties are at the *surface* of the cluster. Thus, the POM species could act as ideal active materials for electrochemical capacitors when combined with acidic electrolytes [14,33]. Contrary to conducting polymers, POMs have not been widely exploited as electroactive materials for supercapacitors. Aside from their use as electrolyte components reported in several patents [34,35], to the best of our knowledge, only our preliminary communication, dealing with the use of POMs as active materials for electrochemical capacitors [33], and a single report describing the device consisting of pure phosphomolybdic acid in one electrode vs. widely used RuO_2 in the other [36] have been published so far.

We report here for the first time the use of hybrid nanocomposite materials formed by polyaniline (conducting polymer) and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ (polyoxometalate) as electrodes for solid state electrochemical capacitors. We describe the electrochemical preparation of carbon electrodes modified with hybrid films formed by the nanosized phosphomolybdic (PMo12) cluster dispersed into polyaniline. The resulting modified electrodes have been used for the fabrication of a solid state electrochemical capacitor cell in which two hybrid polymeric films are separated by a proton-conducting membrane of poly(2,5-benzimidazole) (ABPBI) doped with phosphoric acid. This symmetrical device allows for the use of the phosphomolybdate–polyaniline hybrid as a doubly active nanocomposite material (in which both the organic and inorganic components are electroactive).

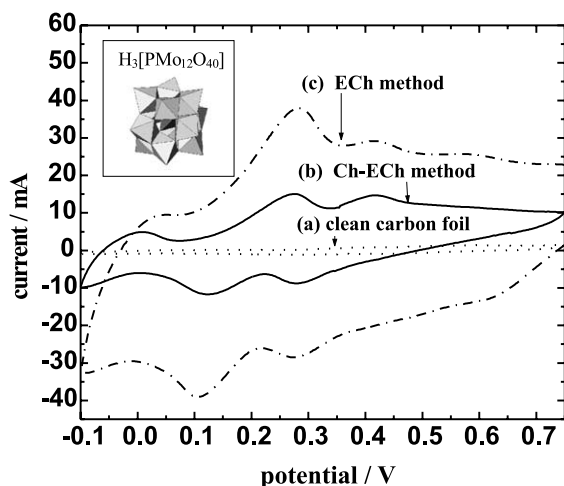


Fig. 1. Cyclic voltammograms of (a) bare carbon foil electrode, (b) a hybrid film deposited on carbon foil by using Ch–ECh method, and (c) a hybrid film deposited on carbon foil by using ECh method. Electrolyte, $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; scan rate, 20 mV s^{-1} . (Ag/AgCl reference electrode)

Preliminary tests show that the symmetrical cell can be cycled at least for as many as 2000 cycles.

2. Experimental

Phosphomolybdic acid and aniline were obtained from Fluka. All other chemicals were reagent grade purity, and were used as received. Solutions were prepared using deionized water. Experiments were carried out at room temperature ($20 \pm 2^\circ \text{C}$).

Electrochemical measurements were done with PAR273A potentiostat (Princeton, USA). A standard three electrode cell was used for the preparation of films and for electrochemical measurements. The working electrode for cyclic voltammetric measurements was a carbon foil (Goodfellow, Cambridge, UK) of 4 cm^2 geometric area, and the counter electrode was made from Pt wire. All potentials were measured and expressed vs. the Ag/AgCl reference electrode.

The hybrid electrodes were prepared as thin films on carbon foil using two methods. In a combined chemical–electrochemical (Ch–ECh) method, the powder obtained from the direct reaction of 5 g of PMo12 and 1 cm^3 of pure aniline was first dissolved in 100 cm^3 of $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The resulting solution was further used for the electrodeposition of a hybrid film onto a carbon foil by performing 12 full potential cycles at 1 mV s^{-1} in the range of potentials from -0.1 to 0.85 V . A second direct electrochemical method (ECh) involved only repetitive potential cycling (12 full voltammetric cycles at 1 mV s^{-1} from -0.1 to 0.85 V) of carbon foil substrate in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ containing $0.013 \text{ mol dm}^{-3} \text{ PMo12}$ and 0.2 mol dm^{-3} aniline in the potential range.

The electrode materials were assembled as disks (geometric area, 0.8 cm^2) into a redox capacitor half-cells placed within Swagelok holders. They were tested using a multichannel charge–discharge galvanostatic analyzer (Arbin Instruments, College Station, USA) in the potential ranges from 0 to 0.5 V or from 0 to 0.8 V .

A separator was in a form of the solid electrolyte membrane synthesized as an adduct of ABPBI (polybenzimidazole) and phosphoric acid. It contained on average, 2.8–3.0 molecules of H_3PO_4 per each repetitive unit of polymer. The thickness of the membrane was approximately $20 \mu\text{m}$.

Surface examination of hybrid films was done using JEOL Model JSM-5400 scanning electron microscope.

3. Results and discussion

Fig. 1 illustrates the cyclic voltammetric responses of (a) bare carbon foil, (b) carbon foil modified with hybrid film using Ch–ECh method, and (c) carbon foil modified with hybrid film using ECh method. It is apparent from

these experiments that, under the same electrodeposition conditions, the electrochemical method (Curve c) tends to produce thicker hybrid films characterized by higher currents in comparison to the chemical method (Curve b). The data of Fig. 1 are also consistent with the combined activity of both organic polymer and inorganic cluster in the hybrid film. In view of the previous reports [20,21], the increased voltammetric currents at potentials more positive than 0.45 V (Fig. 1, Curves b and c) shall be assigned to the redox behavior of emeraldine, the partially oxidized form of polyaniline. The reduction and oxidation peaks at about 0.3 and 0.4 V, respectively, reflect the first (most positive) two-electron redox reaction of PMo12. The dominating set of peaks appearing in the potential range from 0.1 to 0.3 V originates from the overlapping of two processes, the second (more negative) two-electron redox reaction of PMo12 and the emeraldine/leucoemeraldine major reaction of polyaniline. At potentials more negative than 0.05 V, the third reduction process of PMo12 starts to appear.

Another important feature of the work reported here was the use of a novel proton-conducting membrane to form a practical solid state device. The actual capacitor cell was assembled by sandwiching a proton-conducting polymer electrolyte membrane in between two identical hybrid film electrodes fabricated as described above. The solid electrolyte membrane (approximately 20 μm thick) was an adduct of ABPBI (poly-2,5-benzimidazole) and phosphoric acid (2.8–3.0 molecules of H_3PO_4 for repetitive unit of polymer).

Following assembling, the symmetrical electrochemical cells, consisting of hybrid film electrodes and an ABPBI membrane in between, were subjected to diagnostic experiments in which current–potential tests were performed in two-electrode mode (Fig. 2). The voltammetric currents observed were higher in the case of a system utilizing hybrid film electrodes prepared using direct electrochemical (ECh) method (Curve c) rather than the system produced by combined chemical–electrochemical (Ch–ECh) method (Curve b). This result is in agreement with the voltammetric data of Fig. 1 where the responses of the respective modified electrodes are compared. Furthermore, when the surfaces of these electrodes were examined using scanning electron microscopy (SEM), it became evident from the images that the hybrid film fabricated by ECh method (Fig. 3(B)) constitutes a much more microporous material in comparison to the film deposited using Ch–ECh approach (Fig. 3(A)). Thus, despite the fact that the ECh-produced films are thicker, they are also likely to facilitate better charge transfer at the interface with supporting electrolyte.

Finally, the hybrid films were tested in a redox capacitor cell assembled within a Swagelok holder. The charging–discharging characteristics were recorded

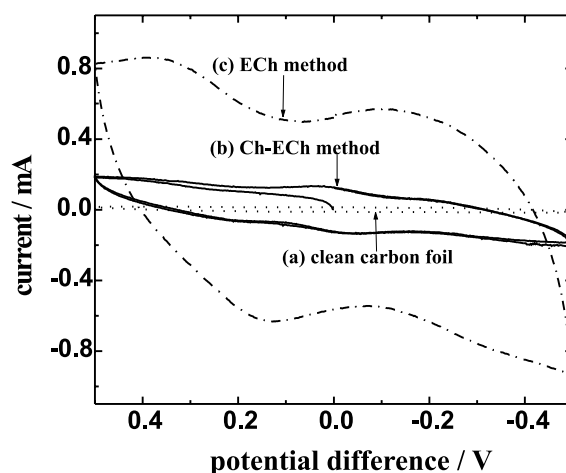


Fig. 2. Current–potential responses (recorded in two-electrode mode) of symmetrical capacitor cells containing (a) two bare carbon foil electrodes, (b) two carbon foil electrodes modified with hybrid films deposited by using Ch–ECh method, and (c) two carbon foil electrodes modified with hybrid films deposited by using ECh method. Voltammetric cycling started from 0 V. Scan rate 20 mV s^{-1} . The separator used was ABPBI (polybenzimidazole) membrane with phosphoric acid.

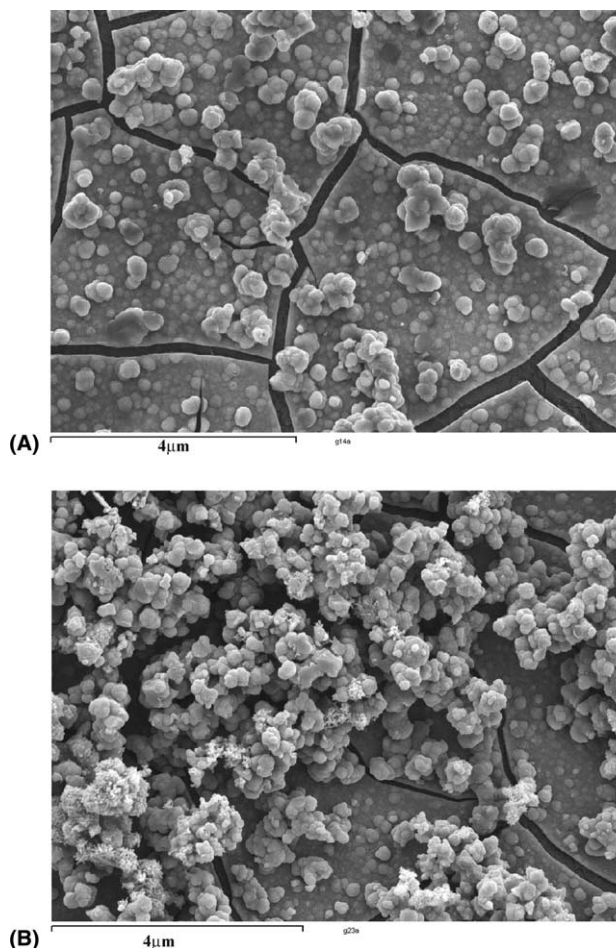


Fig. 3. Scanning electron micrographs of (A) a hybrid film deposited on carbon foil by using Ch–ECh method, and (B) a hybrid film deposited on carbon foil by using ECh method.

using a multichannel galvanostatic cycler in the potential range from 0 to 0.5 V (or from 0 to 0.8 V) at various current densities (from 0.05 to 5 mA cm⁻²). For the sake of clarity, we present here only the results concerning the behavior of hybrid films obtained by the preferred ECh method. Furthermore, we report the results based on area normalization, rather than normalization per unit of mass, because the latter approach was impractical in the case of these electrochemically deposited thin films.

Fig. 4 illustrates typical charging–discharging cycles of the capacitor recorded at a current density of 1 mA cm⁻². The observed charging–discharging profiles were close to linear, and this characteristics did not change even when the potential limit was extended from 0.5 to 0.8 V (for conciseness not shown here). Under current densities of 0.125 mA cm⁻², the average capacity determined in repeating cycles was 195 mF cm⁻² which corresponded to an energy density of 24.4 mJ cm⁻². As expected, the effective capacity decreased upon application of increasing current densities (Fig. 5): following an initial rapid decrease a leveling effect was observed at current densities exceeding 1.5 mA cm⁻², and capacity values started to oscillate around 50 mF cm⁻².

Although no attempt was made to optimize the construction of the electrochemical capacitor, the parameters obtained here make the system potentially attractive for the accumulation of charge with the use of electrodes modified with thin redox hybrid films [33,37,38]. The results could get further improved by optimization of the thickness and morphology of the microstructure of the active material deposited. Further research is along this line, but even the present results constitute a remarkable example of a novel working concept in energy storage materials by showing the possibility to harness the electrochemical activity of polyoxometalates anchored in hybrid materials for application in electrochemical capacitors.

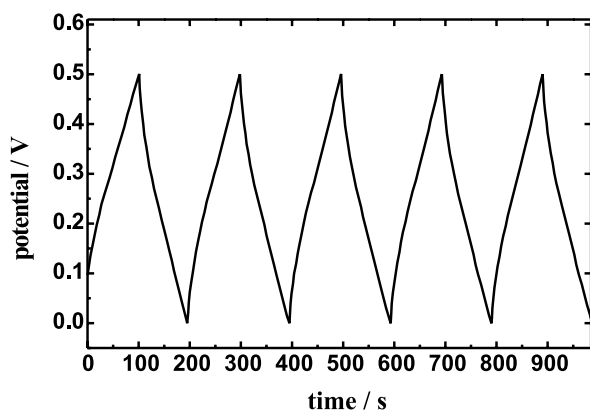


Fig. 4. Galvanostatic (current, 1 mA cm⁻²) charging–discharging of a symmetrical electrochemical capacitor utilizing two carbon foil electrodes modified with hybrid films deposited by using ECh method. The separator was ABPBI membrane with phosphoric acid.

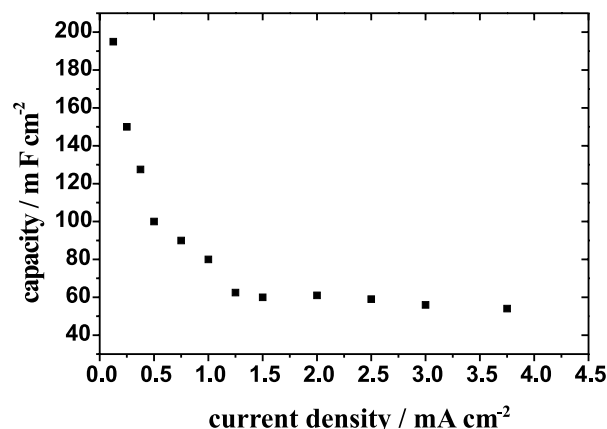


Fig. 5. Dependence of capacity on increasing current densities. Potential range, 0–0.8 V. Other conditions as for Fig. 4.

Indeed, an important issue of this work is that, in striking contrast to the limited cycling capability of the device utilizing hybrid organic–inorganic films in non-aqueous (Li⁺) electrolytes, the present capacitor cell showed a sustained cyclability over a fairly long period of time and cycles. Fig. 6 illustrates the dependence of effective capacity over several hundred cycles. It should be noted that these cycles were measured after the experiments at different current densities shown in Fig. 5. Following a moderate initial decrease that occurred within the first 100 cycles, capacity values remained essentially unchanged upon further cycling.

We found that our system could stand up to 2000 cycles while showing only a small (10–15%) decrease in capacity, illustrating the sturdy nature of these hybrid materials in energy storage applications and showing the potential for the concept of hybrid integration of nanometric clusters and molecular species in the design of novel functional materials.

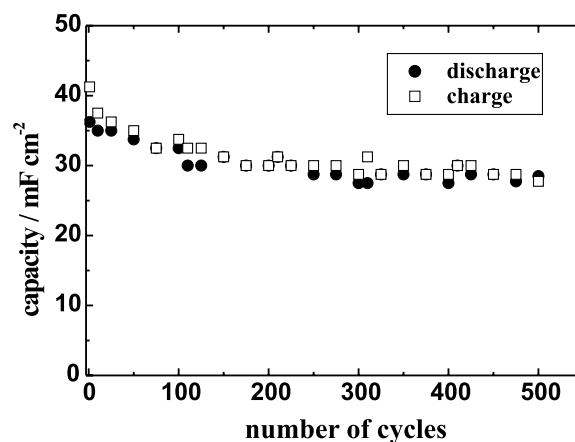


Fig. 6. Dependence of capacity on the number of charge–discharge cycles. Current density, 1 mA cm⁻². Potential range, 0–0.8 V. Other conditions as for Fig. 4.

4. Conclusions

The present work demonstrates the usefulness of organic–inorganic hybrid materials for energy storage in electrochemical capacitors. In this hybrids the nanometric inorganic clusters are anchored in the material due to the existence of electrostatic interactions between anionic phosphomolybdate and positively charged doped polyaniline [20,21]. The present application exploits the electroactivities and the good protonic conductivities of both polyoxometalate clusters and the organic polymer matrix as components of the hybrid film. Another important issue is that the Keggin type heteropolymolybdate provides mixed-valence redox centers between which fast electron hopping (self-exchange) is feasible [1,33]. The fact, that the phosphomolybdate redox processes appear mostly in the potential range where polyaniline is conductive, facilitates delivery of charge and allows the hybrid material to behave reversibly and reproducibly in a proton-conducting electrolyte. The whole concept communicated here may lead to the fabrication of novel stable organic–inorganic hybrid films that show high current densities at electrochemical interfaces and are capable of effective accumulation and mediation of charge.

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