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Aqueous solutions of acidic ionic liquids for enhanced stability of polyoxometalate-carbon supercapacitor electrodes

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HIGHLIGHTS

- Polyoxometalates nanoconfined in microporous carbons were synthesized.
- Protic ionic liquids electrolyte dramatically improves cycling stability.
- Specific capacitance of carbon increased by ~90% with polyoxometalates' addition.

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ABSTRACT

Nanocomposites based on polyoxometalates (POMs) nanoconfined in microporous carbons have been synthesized and used as electrodes for supercapacitors. The addition of the pseudocapacitance from highly reversible redox reaction of POMs to the electric double-layer capacitance of carbon lead to an increase in specific capacitance of ~90% at 1 mV s⁻¹. However, high solubility of POM in traditional aqueous electrolytes leads to rapid capacity fading. Here we demonstrate that the use of aqueous solutions of protic ionic liquids (P-IL) as electrolyte instead of aqueous sulfuric acid solutions offers an opportunity to significantly improve POM cycling stability. Virtually no degradation in capacitance was observed in POM-based positive electrode after 10,000 cycles in an asymmetric capacitor with P-IL aqueous electrolyte. As such, POM-based carbon composites may now present a viable solution for enhancing energy density of electrical double layer capacitors (EDLC) based on pure carbon electrodes.

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1. Introduction

Improvement in electrical energy storage (EES) technologies is one of the most critical issues and has attracted a considerable interest in both academia and industry [1–3]. Electrochemical capacitors also known as supercapacitors are promising devices for highly efficient energy storage and rapid power delivery [4–6], occupying the gap between batteries and dielectric capacitors on the Ragone plot. The energy storage mechanisms in supercapacitors can be broadly classified into (i) charge accumulation in electrical double layers (EDL) (usually on high surface area porous carbon) and (ii) reversible redox processes (usually on the surface

of transition metal oxides or conducting polymers). Commercial supercapacitors typically utilize EDL for charge storage, which somewhat limits their volumetric and gravimetric capacitance and require substantial improvements to meet nowadays rapidly growing demands [7]. One of the strategies for such improvements is the development of hybrid composite materials, where both EDL capacitance and redox activity-induced pseudo-capacitance co-exist.

Polyoxometalates (POMs) are clusters of metal oxide units, comprising a large diversity of microstructures and a vast array of chemical and physical properties, which have been studied in various fields such as energy storage, catalyst, magnetic, and electrochromic applications, to name a few [8]. POMs have been tested for use in lithium ion batteries (LIBs) [9–12] and more recently in supercapacitors [13–16] due to POM's reversible redox activities.

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Unfortunately, almost all POMs are of a small size and suffer from a high solubility in polar solvents, especially in aqueous solutions of acids [17]. A relatively recent study has shown that POMs can be absorbed in the pores of electrically conductive microporous carbons [18]. We shall note that microporous activated carbons (AC) remain the material of choice for industrial fabrication of supercapacitors, due to AC's low cost, abundance, high electrical conductivity, large specific surface area (SSA), excellent chemical and thermal stabilities [1,6,19–21]. Since pure AC are already used by supercapacitor industry, their replacement by POM-infiltrated AC would not require significant modifications in the electrode preparations and cell assembling. The broad range of chemical compositions available in POMs is also attractive for optimizing the redox potentials in anode and cathode compositions to achieve high average voltage and high energy density in full cells. However, the biggest challenge of preventing POM dissolution and cell degradation must first be resolved.

The applications of protic ionic liquids (P-IL) are rapidly growing as they offer attractive physical and chemical properties, such as good thermal stability, high ionic conductivity and wide electrochemical stability window, to name a few [22–24]. Several recent studies demonstrated good electrochemical performances of protic ionic liquids [25–27]. Here we demonstrate for the first time that replacing conventionally used aqueous solutions of inorganic acids (such as H_2SO_4) by aqueous solutions of P-IL offers an opportunity to significantly enhance stability of POM-infiltrated ACs. The POM-AC composites showed virtually no degradation in capacitance during 10,000 cycles in P-IL comprising aqueous electrolytes. This is in a sharp contrast to the same composite electrodes losing over 70% of the capacitance after 2000 cycles in a regular H_2SO_4 -based electrolyte.

2. Experimental details

2.1. Material synthesis

All the chemical reagents were directly used without any purification. 5 mL of a 10 mM phosphomolybdic acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ (PMo_{12}) (Sigma-Aldrich) was infiltrated into 100 mg of a porous activated carbon. The suspension was stirred vigorously for 24 h, then washed with large amount of deionized (DI) water, filtered off and dried under vacuum at 80 °C for at least 12 h. The composite products were labeled as AC@PMo_{12} .

2.2. Material characterizations

The X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo K Alpha spectrometer with an Al K-alpha source. A pass energy of 50 eV was used with 0.1 eV resolution and a 50 ms collection time per point, repeated 10 times and averaged for the detailed scans. A pass energy of 200 eV was repeated 3 times for survey scans in order to obtain the atomic composition. X-ray diffraction (XRD) measurements were performed using a Panalytical X'Pert PRO Alpha-1 diffraction system (Pananalytical, Almelo, Netherlands), with peaks collecting from $2\theta = 10^\circ$ to 70° and a step size of 0.02° .

The morphology was characterized by using a LEO 1530 scanning electron microscopy (SEM) microscope (LEO, Osaka, Japan, now Nano Technology Systems Division of Carl Zeiss SMT, MA, USA) coupled with an energy-dispersive X-ray (EDX) spectrometer. A transmission electron microscope (TEM) observation and the linear EDX scans of elemental distribution were carried out with Philips CM200UT. The N_2 adsorption isotherms were collected at 77 K using a Micromeritics ASAP 2420 instrument (Micromeritics, USA). Ultra high purity N_2 (99.99%, Airgas, USA) gas was used for all

experiments. Prior to the adsorption measurements, the powder samples were degassed for 3 h at 573 K under vacuum. The specific surface area (SSA) was calculated using the Brunauer, Emmett, and Teller (BET) method with the range of relative pressures from 0.05 to 0.15.

2.3. Electrochemical characterization

Electrodes were prepared by mixing with polytetrafluoroethylene (PTFE) (60 wt % water suspension, Sigma Aldrich, USA) as a binder to form a gum consisting of active material (95 wt %) and PTFE (5 wt %). After drying overnight at 80 °C under vacuum, the electrodes were calendared to the thickness of $\sim 150\ \mu\text{m}$ using a commercial rolling mill and dried in the vacuum oven at 80 °C for at least 12 h to remove moisture. The produced electrode was cut into $\frac{1}{4}$ inch diameter circles, of which the mass was around 2 mg. The initial tests were performed in three-electrode cells with 1 M $[\text{Bmim}]\text{HSO}_4$ aqueous solution as the electrolyte and a Pt foil and a Ag/AgCl as the counter and reference electrodes, respectively. Full cells were assembled in a two-electrode configuration using Ti foils as current collectors and Celgard 3501 membrane (Celgard LLC, US) of $\sim 25\ \mu\text{m}$ in thickness and $\sim 55\%$ porosity as a separator. The counter electrode for two-electrode tests was made from a commercial AC (YP17-D, Kureha, Japan) using the same process. The cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) measurements were carried out using a Solartron 1480A Multi-Stat (Solartron Analytical, USA) with scan rates ranging from 1 to $500\ \text{mV s}^{-1}$. The gravimetric capacitance, C (F g^{-1}), was calculated from three-electrode measurements according to $C_m = Q/(2m\Delta E)$, where C_m (F g^{-1}) is specific capacitance, Q (C) is the integrated charge, and ΔE (V) is the width of potential window, and m is the effective mass (g) of the electrode [28].

3. Results and discussion

To examine the chemical composition, XPS (Fig. 1) was carried out to characterize the surface composition of the produced composite. A survey XPS spectrum for the AC@PMo_{12} (Fig. 1a) indicates the existence of C, Mo, and O elements present in PMo_{12} . The high-resolution XPS spectrum for C1s can be de-convoluted into four peaks (Fig. 1b), where the peaks at 284.6 eV correspond to sp^2 carbon and peaks at 285.8, 288.0, 290.71 eV can be assigned to surface functional groups C–O, C=O and O–C=O, respectively [29]. There appear two evident peaks in Fig. 1c at 232.6 ($\text{Mo}3d_{5/2}$) and 235.7 ($\text{Mo}3d_{3/2}$), characteristic of Mo(VI) in the oxidation state of MoO_3 [11,30]. The binding energy at 530.4 eV is ascribed to the O1s in MoO_3 [31], whereas the residue peak at 531.7 eV is attributed to the residual oxygen-containing groups in AC. For comparison, XPS result of pure AC was shown in Fig. S1. In addition, the corresponding EDX pattern (Fig. S2) analysis agrees well with the composition. The XRD pattern (Fig. S3) of AC@PMo_{12} indicates an X-ray amorphous structure. The Keggin type PMo_{12} only has a small molecular size of 11–12 Å [32] and is anchored to surface sites within the micropores of carbon, thus not forming long range ordered structures.

The adsorption of PMo_{12} into of AC is demonstrated by the isotherms in Fig. 2, where the calculated BET SSA and pore volume was decreased significantly after stirring with a PMo_{12} solution and drying. Such a significant pores volume reduction indicate successful PMo_{12} absorption into carbon micropores.

The morphology of the AC@PMo_{12} was examined by SEM characterization. The AC are spherical particles with diameters ranging from approximately 400 nm to 1 μm (Fig. 3a). The high-magnification image (Fig. 3b) demonstrates that no agglomeration of PMo_{12} particles could be seen on the outer surface of the AC,

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