Facile synthesis of reduced graphene oxide/peroxomolybdate(VI)–citrate composite and its potential energy storage application

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Abstract A new energy storage material based on molybdate active species has been presented. Molybdenum seems to be a perspective material in supercapacitors because of numerous possible metal oxidation states, electrolyte storage by means of various chemical reactions and availability in comparison to other refractory metals. Material synthesized within this research was composed of reduced graphene oxide matrix and peroxomolybdate(VI)–citrate active dimers. It was showed that peroxomolybdate(VI)–citrate structure enhanced electrochemical activity of symmetric supercapacitor. Simple methodology was used to synthesize a composite with pH adjustment as the key step. The specific capacity calculated from galvanostatic charge/discharge curves was as high as 250 F/g. Material was distinguished by good cyclability with 5% capacity loss after 1000 cycles. The increase in charge transfer resistance, induced by metal–oxygen compound within the carbon matrix was relatively low, compared to parent reduced graphene oxide. Amorphous structure of peroxomolybdate(VI)-modified material was observed with slight increase in the interlayer distance in comparison to parent reduced graphene oxide. The height and lateral size of crystallites were also determined. Significant decrease in the specific surface area of peroxomolybdate(VI)-modified composite was observed, in comparison to the parent reduced graphene oxide.

1 Introduction

Transition metal oxides are commonly used in energy storage materials because of relatively high increase in specific capacity through so-called pseudocapacitance, availability, in many cases low price and because of chemical and physical properties [1, 2]. Among them refractory metals (molybdenum, tungsten, rhenium, tantalum and niobium) are rarely taken into account mainly because of economy and low abundance. Molybdenum, tungsten and rhenium may be recognized as potentially effective materials that are able to enhance the specific capacity electrode, which is attributed to numerous oxidation states of these metals. The chemistry of rhenium seems to be out of scope in this matter as it is very rare and expensive metal. However, molybdenum and tungsten are relatively easily available. In this paper, the possibility of molybdenum species application in energy storage materials was examined. Molybdenum has high thermal stability, high thermal and electric conductivity, is corrosion resistant and has low thermal expansion coefficient. This makes it perfect for applications such as electronics, metallurgy, aerospace industry, lighting technologies and coatings [3]. In the literature, numerous examples of molybdenum(IV) oxide and molybdenum(VI) oxide as well as molybdenum(IV) sulfide-based electrodes for supercapacitors and lithium-ion batteries can be found. The specific capacity of these materials may be varied from 36 F/g for MoO_2 to 288 F/g for $\alpha\text{-MoO}_3$ [4]. A perspective material is also molybdenum sulfide that may result in ca. 410 F/g [5]. An important feature of molybdenum is capability to form a lot of various structures that are composed of molybdenum–oxygen bonds. The chemistry of molybdenum compounds is a vast range of different molybdenum–oxygen–hydrogen combinations [6] that may be perfectly suited as pseudocapacitive materials in energy storage. Another

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important class of compounds exhibiting reversible redox activity is molybdates. Their high catalytic activity, good electrochemical properties and environmental friendliness have driven them to energy storage applications [7]. The specific capacity reported for various molybdate-based supercapacitors for single electrode obtained using three electrode system was as high as 65 F/g for $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ nanostructures [8], 170 F/g for CoMoO_4 nanospheres [9], 187 F/g for $\text{MnMoO}_4/\text{CoMoO}_4$ nanowires [10], 200 F/g for $\alpha\text{-MnMoO}_4$ [11], 212 F/g for carbon sphere@ NiMoO_4 [12], and 974 F/g for NiMoO_4 nanorods and nanospheres [13]. While using two-electrode system in a symmetric configuration, 81 F/g was obtained for $\alpha\text{-MnMoO}_4$ [11] and 53 F/g for MoS_2/RGO nanocomposite [14].

In lithium-ion batteries, iron molybdate and tin molybdate can be found [15, 16]. The great attention has been recently attracted to more complex molybdate like copper hydroxy molybdate or zinc-hydroxy molybdate and their potential electrochemical activity [17, 18]. This paper reports facile synthesis of graphene-based peroxomolybdate(VI)–citrate composite. A properly adjusted pH enhanced formation of peroxomolybdate(VI)–citrate dimers $\text{M}_5[\text{MoO}(\text{O}_2)_2\text{-(Hcit)H(Hcit)(O}_2)_2\text{OMo}]\cdot 6\text{H}_2\text{O}$ [19] that were used as pseudocapacitive active species in enhancing non-faradaic reactions.

2 Experimental

2.1 Material preparation

Graphite oxide was prepared using Hummers method [20] by mixing 10 g synthetic graphite with 230 mL 95–97% sulfuric acid (Acros Organics), 5 g sodium nitrate and 30 g potassium permanganate in a round-bottomed flask equipped with a reflux and thermometer and ice-cooled at the temperature close to 273 K. After 8 h, GO slurry was transferred diluted with deionized water, washed several times by decantation and vacuum-filtrated using two filter papers (Munktell, 390). As-prepared GO was dried at 110 °C in an oven. Graphite oxide was then milled in a mortar and ultrasonically dispersed in water. Next, hydrazine hydrate was added, mixture was sonicated and then boiled on a hot plate. Finally it was filtered, washed with copious amount of water and dried at 110 °C. Reduced graphene oxide was denoted as RGrO.

Molybdenum active species was synthesized as follows: 2.4 g $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ was dissolved in 10 ml water, 0.7 ml 30% H_2O_2 was added. Then solution containing 1.9 g citric acid in water was added and the mixture was thoroughly mixed.

Next, reduced graphene oxide was dispersed in 50 ml and pH was adjusted by 1 M HNO_3 to ca. 4.7. Molybdenum precursor was added to reduced graphene oxide and

components were ultrasonically mixed for 15 min and then simultaneously magnetically mixed and boiled. Finally material was vacuum-filtrated using micro-glass filters and dried. 0.17 g product denoted as RedNaCA (Reduced graphene oxide Na-based molybdate and Citric Acid) was obtained.

2.2 Characterization

XRD analysis was performed using Co $K\alpha$ lamp in 2θ range from 10° to 100° (Seifert FPM)—the use of cobalt lamp instead of commonly used copper was imposed by technical problems. BET surface area was analyzed using pore structure analyzer (3Flex™, Micromeritics). SEM analysis was performed using JXA 8230, Jeol, to show the morphology of considered materials. Electrochemical experiments were carried out using two-electrode system presented in Fig. 1.

The working electrode materials were pasted on electrochemical nickel current collectors to form films and separated with glass microfiber membrane (Whatman) soaked with 6 M KOH. The accurate weight of the electrodes was read by a high-precision balance (Mettler Toledo AB 204S). Electrodes, current collectors and separator were pressed by four screws in a poly(methyl methacrylate) (PMMA) casing. Cyclic voltammetry (CV) in 0–1 V window at scan rate 500 mV/s, galvanostatic charge/discharge (GC) at current density in a range 0.1–6 A/g, and electrochemical impedance spectroscopy (EIS) in the frequency range 100 kHz–100 mHz with the amplitude of sinusoidal voltage signal equal to 10 mV were performed with Autolab PGSTAT 302N workstation.

Fig. 1 Test cell for electrochemical analysis

3 Results

Scheme of reduced graphene oxide/peroxomolybdate(VI)–citrate composite preparation is presented in Fig. 2. Process was fast and easy. First, graphite oxide was ultrasonically exfoliated into graphene oxide and then chemically reduced. Second, peroxomolybdate(VI)–citrate complex was prepared by oxidation of sodium molybdate(VI) precursor with concentrated hydrogen peroxide with the addition of citric acid as complexing agent. Both solutions were ultrasonically and magnetically mixed together and boiled. Dry product was visually very similar to parent reduced graphene oxide but electrochemically much different.

XRD patterns of the peroxomolybdate composite and parent reduced graphene oxide are presented in Fig. 3. In both materials, two signals located around 27° and 52° were recorded. These signals were attributed to the

Fig. 3 XRD patterns for RGrO and RedNaCA

Fig. 2 Schematic presentation of reduced graphene oxide/peroxomolybdate(VI)–citrate composite preparation

matrix—reduced graphene oxide; however, it should be emphasized that obtained 2θ angle values are bigger than commonly found in the literature. This was a result of cobalt lamp used in analysis, which caused peak shift to bigger angles with respect to copper lamp (the application of Co $K\alpha$ lamp was pursued by the Analytical Department of Institute of Non-Ferrous Metals responsible for all XRD analyses). Regardless of peak shifts, the localization of signals was appropriate with respect to references. Unfortunately, no strong molybdenum signal was detected that indicates the amorphous structure of the peroxomolybdate(VI)–citrate phase. The analysis performed using ParSize analyzer showed that the interlayer distance for RGrO and RedNaCA was as high as 0.35 and 0.37 nm, respectively, while the theoretical number of graphene layers within material was 31 for RGrO and 29.3 for RedNaCA. The crystallite size (L_c —crystallites height and L_a —lateral size) of graphene domains calculated using

Sherrer equation was as high as 11.1 and 19.9 nm for RGrO and 10.5 and 18.7 nm for RedNaCA.

The specific surface area evaluated for both materials was 26.2 m²/g for RGrO and merely 4.4 m²/g for RedNaCA. Low surface area of the composite is in accordance with assumptions as the material was obtained in reaction of reduced graphene oxide with molybdenum precursor, which might partially clog the pores.

Morphological studies were performed using scanning electron microscopy. Results are presented in Fig. 4.

Amorphous phase of embedded peroxomolybdate–citrate complex as well as low magnification of the microscope did not allow to observe specific molybdenum particles within the graphene layer. It was found that for parent reduced graphene oxide slightly more corrugated structure was reported that may indicate clogging of interlayer spaces of RedNaCA by active material. This is in accordance with the specific surface area data.

Fig. 4 SEM images recorded for RedNaCA (a, c) and RGrO (b, d) at magnification $\times 500$ and $\times 5000$

Results of the electrochemical tests performed using reduced graphene oxide and its composite with peroxomolybdate-citrate are presented in Fig. 5. The most credible method to evaluate the specific capacity of the prepared material is galvanostatic charge/discharge characteristic. The specific capacity was calculated using the following formula: $C_{SP} = i \times t / (m \times \Delta V)$, where C_{SP} is the specific capacity, i is the current intensity, t is the discharge time, m is the mass of active material, and ΔV is the potential difference.

Both materials were examined using current density range from 0.1 to 6 A/g. The recorded specific capacity (Fig. 5a) was as high as 147 F/g for a parent RGrO and 250 F/g for RedNaCA. Charge and discharge curves were ideal-like symmetrical; however, for RedNaCA no apex curvature was observed and material was able to discharge completely. Cyclic voltammetry was used to determine the capacity loss during 1000 cycles. Electrodes were swept with a potential at a scan rate 500 mV/s in a potential window 0–1 V, the most common for aqueous electrolyte. Although not very much resembling box-like shape (rounded edges), CV curves were symmetric with an acceptable value of recorded current intensity (Fig. 5b). This indicates reversibility of electrode processes; however, some barriers were present that impeded charge and discharge. Slightly enhanced reactions' reversibility was reported for RedNaCA with a longer plateau

region in the range 0.4–1 V (charging) and 0.55–0 V (discharging). Some shape imperfections with respect to ideal box-like shape may result from improper pore distribution of required size or some spatial obstacles within material caused by active species, which was synthesized within pores. A decrease in the specific capacity after 1000 cycles, calculated from CV curves, was 5 and 7% for RedNaCA and RGrO, respectively (Fig. 5c). The relation of real impedance vs imaginary impedance was presented in the form of Nyquist plot (Fig. 5d). Generally, such curves are composed of two-component semicircle over the high-frequency region corresponding to the Faradaic charge transfer resistance and linear part in a low-frequency region indicating a pure capacitive behavior and representing the ion diffusion in the electrode structure. These data allowed to estimate electrolyte resistance R_s , which was 0.13 and 1.25 Ω for RedNaCA and RGrO, respectively, and charge transfer resistance R_{CT} , 2.07 and 1.1 Ω , respectively. This slightly bigger value of R_{CT} was responsible for slower kinetics. Smaller loop and 45° curve in the low-frequency region are attributed to the better Warburg diffusion caused by improved mass transfer from the electrolyte to electrode interface. As there was no significant “chemical obstacles” within RGrO the net real impedance value (10 Ω) was slightly lower in comparison to the RedNaCA (15 Ω).

Fig. 5 Results of electrochemical tests: **a** galvanostatic charge/discharge (RedNaCA—green, RGrO—brown), **b** cyclic voltammetry curves at scan rate 500 mV/s, **c** capacity loss calculated from CV curves and **d** Nyquist plots at frequency range 100 k Ω –100 m Ω

4 Conclusions

A new type of peroxomolybdate(VI)–citrate structure synthesized within reduced graphene oxide matrix using simple pH adjustment method was developed. It was demonstrated that peroxomolybdate(VI)–citrate species effectively enhanced specific capacity of reduced graphene oxide. Specific capacity obtained from galvanostatic charge/discharge curves for composite material was as high as 250 F/g, i.e., about 100 F/g more than for parent reduced graphene oxide. Cycling stability was also improved with the capacity loss after 1000 cycles at the level merely 5%. Although an increase in charge transfer resistance was observed, the net impedance relation for composite material was advantageous with respect to the matrix (smaller loop and more steep curve). It was found that embedded peroxomolybdate(VI)–citrate species resulted in a decrease in specific surface area, by partial clogging of matrix pores. Although slightly increased interlayer distance was observed for the composite the theoretical number of layers as well as crystallites size was smaller in comparison to the reduced graphene oxide.

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