Comparison of reducing agent for reduced graphene oxide as cathode for zinc-ion hybrid capacitors

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Abstract. The comparative study of using the different reduced graphene oxide sources, obtained from thiourea and l-ascorbic acid as reducing agent, for zinc cathode capacitors is investigated. The chemical structure and the surface morphology of both reduced graphene oxide samples are examined by infrared spectrum and scanning electron microscopy, respectively. Serving as cathode for zinc-ion hybrid capacitors, the as-prepared reduced graphene from l-ascorbic acid reveals the better the specific discharge capacity (41.50 mAh g⁻¹) than that of the obtained from thiourea (40.78 mAh g⁻¹). The cycle stability of zinc-ion hybrid capacitors coin cell in 2M ZnSO₄ electrolyte is examined by multi-cycles of GCD at 0.1 A g⁻¹, demonstrating that rGO obtained from l-ascorbic acid can endow the retention up to 72.8% after 200 cycles, while rGO obtained from thiourea is remained at 63.1%.

1. Introduction

Nowadays, energy storage devices and electric vehicles have rapidly developed and set high demands for energy density and power density. Supercapacitors possess a fast charge-discharge rate, and high-power density but their low energy density limits their large-scale applications. In contrast, batteries reveal high-energy-density but low energy power, poor rate performance and inferior cycling stability [1]. To overcome these disadvantages of supercapacitors and batteries, the concept of hybrid capacitors has been developed consisting of a battery-type faradaic electrode as an energy source and a capacitive electrode as a power source. Zinc-ion hybrid capacitors (ZICs) have been increased attention in recent progress for many researchers due to high safety, low cost, abundant zinc resource, low redox potential of zinc and high volumetric capacity. In addition, the energy power of ZICs strongly depends on the Zn²⁺ storage behaviors in cathode materials [2]. Several cathode materials have been developed for ZICs, including conductive polymers and carbon materials.

Considerable much effort has been devoted to developing the carbon materials for ZICs such as activated carbon, carbon nanotubes, graphene and so on. Among them, graphene is a material having one atomic thickness materials that consist of sp² hybridized carbon atoms arranged in a honeycomb lattice, becoming a popular topic in material science because of its amazing characteristics such as
excellent structural, large surface area, mechanical, thermal, and electrical properties [3] with talented applications in the field of batteries, catalyst supports, nanoelectronics, composites and supercapacitors. Commonly, monolayer graphene sheets can be synthesized in large quantities by chemical reduction or thermal treatment of graphene oxide (GO). Graphite powder can be used as precursor to synthesize GO and reduced graphene oxide (rGO), respectively. After graphite powder oxidation under acid condition, the functional groups of oxygen were created between multi-layers of carbon sheet. The GO layers were mostly bonded with epoxy, hydroxyl groups. While carboxyl and carbonyl groups were bonded the rim of the layer [4]. These oxygens containing functional groups change the GO van der Waals interaction, making it hydrophilic and exfoliating in an aqueous solution. Thus, GO is greatly stable dispersion in other polar organic solvents and water.

One of the effective methods is exfoliation of GO by ultrasonication to obtain exfoliated GO before chemical reduction process [5]. However, when the functional groups of oxygen were removed to get the graphene sheets, its losses the ability to dispersed in water and agglomeration will be occurred. The different reducing agents were applied to synthesize rGO from GO via chemical reduction such as sodium borohydride, hydrazine, hydrazine monohydrate and hydrogen sulfide [6,7]. All these reducing agents are hazardous. In view of this, the present investigation has been focused on the use of thiourea and l-ascorbic acid as a reducing agent. Comparing to other reducing agents, thiourea and l-ascorbic acid are more environmental-friendly. rGO prepared by this method possesses promising electrochemical properties, which can be used as cathode for ZICs applications. Therefore, in this research, the development of graphene as a capacitive cathode for ZICs are proposed, expecting to possess a high power/energy density and long cycle life.

2. Experimental Section

2.1. Materials
Graphite powder was purchased from Sigma-Aldrich Co., Ltd. All other chemicals used were reagent-grade products.

2.2. Synthesis of graphene oxide
Graphene oxide (GO) used in this work was synthesized by oxidation of graphite powder through the modified Hummer’s method [8].

2.3. Synthesis of reduced graphene oxide with thiourea and l-ascorbic acid
GO was dispersed in deionized water at 1 mg/ml by sonication for 30 min. Then, thiourea or l-ascorbic acid as a reducing agent was added into the dispersed GO solution and continually sonicated for 30 min. The suspension was hydrothermal at 120 °C for 3 h. The obtained product was washed several times with deionized water and dried in freeze dry for 24 h.

2.4. Structural and chemical characterization
The chemical structure and surface morphology of samples were characterized by Fourier transform infrared spectrometer (FTIR, Nicolet 6700, using KBr pellets in the 4000-500 cm⁻¹ region) and scanning electron microscopy (SEM, Quanta 250), respectively.

2.5. Electrode assembly and electrochemical testing
The cathode was fabricated by mixing 80 wt.% of active material (rGO-thiourea or rGO-l-ascorbic acid), 10 wt.% of conductive carbon and 10 wt.% of polytetrafluoroethylene (PTFE) binder in ethanol solvent under stirring to form slurry. After that the slurry was pasted onto a graphene foil substrate. The as-prepare cathode samples were dried in air at 60°C for 24 h. Then, punched the cathode samples into a disk and assembled into CR2032 type coin cell with zinc foil as anode, glass fiber as separator, and 120µL 2M ZnSO₄ as electrolyte. The electrochemical properties of the electrode materials were evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). CV measurements
were studied by applying scan rate at 5 mV s\(^{-1}\) and GCD method was used at 0.1 A g\(^{-1}\). In addition, cycle stability was plotted by specific discharge capacity at 0.1 A g\(^{-1}\) for 200 cycles.

3. Results and discussion

3.1. Morphology study

FT-IR spectra are used to elucidate the functional groups of GO, rGO-thiourea and rGO-l-ascorbic acid. As seen in figure 1, the FT-IR spectrum of GO clearly shows the absorption band at 1722 cm\(^{-1}\) assigning to the stretching vibration of C=O in the carboxylic groups. The vibrational bands at 3427 and 1619 cm\(^{-1}\) are ascribed to the stretching vibration of hydroxyl group (-OH). Obviously, it is clear that the reduction process via hydrothermal of GO with l-ascorbic acid can eliminate the oxygen functional groups on GO. While the using of thiourea still remains the partial oxygen function groups as the present of the low intensity peak of 3427, 1722 and 1619 cm\(^{-1}\), confirming the better efficiency of l-ascorbic acid as reducing agent for GO.

![Figure 1. FT-IR spectra of GO, rGO-thiourea and rGO-l-ascorbic acid](image)

The surface morphology and microstructure of the rGO-thiourea and rGO-l-ascorbic acid are characterized by SEM observation. As shown in figure 2a, rGO-thiourea shows the portion of 2D structure sheet coexisting with the twist sheet structure. In contrast, rGO-l-ascorbic acid reveals the sheet-to-sheet separation with 3D porous microstructure as seen in figure 2b, expecting to improve to facilitate ion diffusion and transport of electrolyte on surface [9].

![Figure 2. SEM image of (a) rGO-thiourea and (b) rGO-l-ascorbic acid.](image)
3.2. Electrochemical properties

To evaluate the ZICs efficiency of rGO-thiourea and rGO-l-ascorbic acid, CV measurement is employed to characteristic of ZICs using CR2032 cell battery at 5 mV s\(^{-1}\) with a voltage window of 0.0 V to 1.6 V in 2M ZnSO\(_4\). As shown figure 3a, CV curve of rGO-l-ascorbic acid sample obviously shows a little cliff of redox peak at 1.2 V, considering as the formation of Zn\(^{2+}\) insertion into the rGO-l-ascorbic acid structure on cathode. In fact, the oxidation peak at 1.1-1.2 V is ascribed to the Zn\(^{2+}\) insertion on cathode, accompanied by the reduction of Zn\(^{2+}\) to zinc on anode [10]. In contrast, as shown on figure 3b for CV of rGO-thiourea, the redox peak was unidentified in both of reduction and oxidation curves, indicated the lower adsorption/desorption of Zn/Zn\(^{2+}\) for rGO-thiourea. Notably, the CV results are corresponding to SEM results, confirming that 3D structure of rGO-l-ascorbic acid can facilitate more Zn\(^{2+}\) adsorption/desorption than that of 2D structure of rGO-thiourea.

![Figure 3.](image)

Figure 3. CV curve at scan rate 5 mV s\(^{-1}\) of (a) rGO-l-ascorbic acid and (b) rGO-thiourea.

The galvanostatic charge/discharge curves (GCD) of the rGO-l-ascorbic acid and rGO-thiourea are further investigated as shown in figure 4a. Both of rGO-l-ascorbic acid and rGO-thiourea can accommodate Zn\(^{2+}\) adsorption/desorption during charge/discharge process for ZICs, revealing the unsymmetrical triangular curves. rGO-l-ascorbic acid can achieve the discharge capacity of 41.5 mAh g\(^{-1}\), while rGO-thiourea yields the discharge capacity of 40.78 mAh g\(^{-1}\). The cycling stability of the rGO-l-ascorbic acid and rGO-thiourea are shown in figure 4b. The rGO-l-ascorbic acid can remain more than 72% of its initial capacity even the cycle number extended to 200 cycles at current density of 0.1 A g\(^{-1}\), indicating the excellent cycling stability.

As a comparison, the capacity retention of the rGO-thiourea at 0.1 A g\(^{-1}\) is 63.1% after 200 cycles. Considerably, the structure stability of the rGO-l-ascorbic acid is superior to the rGO-thiourea. This might be because of the fact that 3D framework rGO-l-ascorbic acid structure can remain stability of structure during charge/discharge process, while 2D stacking graphene structure of the rGO-thiourea are collapsed and decrease space in the structure that interrupted Zn\(^{2+}\) adsorption/desorption process.

![Figure 4.](image)

Figure 4. (a) GCD curve at current density 0.1 A g\(^{-1}\) and (b) cycle stability of rGO-l-ascorbic acid and rGO-thiourea at current density 0.1 A g\(^{-1}\).
4. Conclusion
In conclusion, the present study demonstrates that the using of l-ascorbic acid exhibits an excellent reducing performance than that of the using thiourea. The obtained rGO-l-ascorbic reveals a high stability 3D framework of graphene structure, enhancing the cyclic stability (retention of 72.8% after 200 cycles). Reversible ion adsorption/desorption on rGO cathode and Zn$^{2+}$ deposition/stripping on Zn anode enables the ZICs to repeatedly and rapidly store/deliver electrical energy.

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