Os-Ru/Graphene nanostructure for high-performance flow energy systems

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Highlights

- Os-Ru alloy self assembly monolayers on graphene.
- High capacitance retention.
- Pseudocapacitive activities and very high specific capacitance.
- Slurry electrodes in a flow energy system.

1. Introduction

Energy generation from renewable sources such as solar and wind energy is more and more required, to decrease greenhouse gas emissions and fossil fuels consumption. Considering the intermittence and variability of renewable energy sources large-scale and highly efficient energy storage systems, able to quickly respond to large and rapid fluctuations, are crucial to enhance the renewable energy sources exploitation. For the practical application of large-scale energy storage, novel technologies, having major advantages of both electrochemical capacitors and batteries, are required. Energy storage systems common electrodes include carbon based materials (e.g. activated carbon, carbon nanotubes, graphene, etc.), transition-metal and metal oxides, conducting polymers and composites of these materials [1]. Thanks to their high conductivity, electrochemical stability and ability to electrons transport, noble metals have attracted increasing attention in the field of electrode materials [2]. Noble metals usually include the platinum group metals (ruthenium, rhodium, palladium, osmium, iridium, platinum), silver and gold [3]. On the other hand, among noble metals, ruthenium, rhodium, palladium, platinum, silver and gold have been studied as electrode for energy storage system [3]. However, due to the scarcity and high cost of noble metals, the integration with other more sustainable and cheaper materials is critical to minimize their consumption, maintaining or enhancing their performance. Among stable and precious metals osmium has not been studied for these applications. Here, we report a one-step simple synthetic strategy for the preparation of a multifunctional nanostructures made of graphene supporting Os-Ru alloy nanoparticles (Os-Ru/Graphene). Particular attention has devoted to search for a low noble metal content. The nanomaterials, characterized by very small (~ 2 nm) osmium and ruthenium alloy nanoparticles (NPs) grown directly on the graphene surface, take advantages of the synergistic effect of the different components. On the other hand, there is an urgent need to increase grid efficiency and assist implementation of renewable energy sources. For this reason the activity of Os-Ru/Graphene nanostructure was investigated in an energy flow system, decoupling the energy storage capacity from the power delivery rate.

2. Methods

A one-step synthetic strategy [4] for the preparation of Os-Ru/Graphene nanostructures was performed by thermolysis of suitable precursors in organic solvent. To reduce the organic chains amount covering the nanoparticles, Os-Ru/Graphene annealed were obtained after a thermal treatment of the synthesized samples under an air flow. A wide characterization of our nanostructures, before and after the thermal treatment was performed. Raman Spectroscopy, Transmission Electron Microscopy, Thermogravimetric analysis (TG-DTG), XPS characterization and X-ray diffraction were employed. Os-Ru/Graphene nanostructures were used for the preparation of slurry electrodes at different concentrations. Electrochemical tests were performed using a symmetric two-electrode electrochemical cell with equal masses in both electrode suspensions. Nafion-117 membrane was used as a separator between the two slurry electrodes with slurry

diffusion layers on both sides using appropriate gaskets. Cyclic voltammetry (CV) at different scan rates, charge/discharge tests and electrochemical impedance spectroscopy experiments were performed at room temperature using a potentiostat/galvanostat (Autolab PGSTAT 302N). Capacitance values were normalized by the weight of the material in a single electrode, allowing a direct comparison with conventional electrodes, which are also normalized to the content of the active material in one electrode.

3. Results and discussion

A schematic illustration and a photograph of the energy flow system used are shown in the Figures 1a and 1b. This system enables the charging of uncharged and the discharging of previously charged slurry at the same time. This feature is of particular importance to simultaneously respond to fast fluctuations in energy production and energy consumption, which are two inherently independent parameters. In the flow energy system, each electrode consists of a flowable material (Figure 1c) that is produced by mixing nanostructures into an aqueous electrolyte. Enhanced overall capacitance is achieved due to the combination of: (i) electrical double layer (EDL) capacitance on graphene, where the reversible electrostatic accumulation of ions leads to the formation of an EDL by counterbalancing the surface charges of porous electrodes; and (ii) the pseudocapacitance provided by the redox reaction of the Os-Ru NPs. The electrode material retains ~ 97% of their initial capacitance after 200000 cycles, indicating excellent stability and long cycle life.

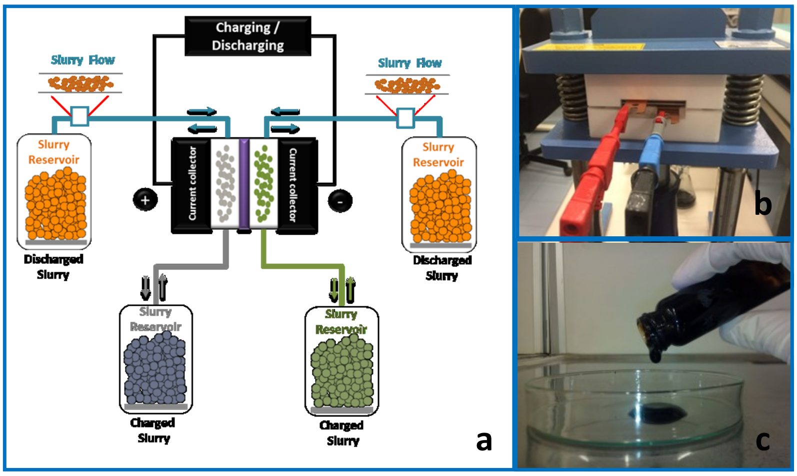

Figure 1. Photo (a) and schematic illustration (b) of the flow energy system. Photo of a prepared slurry (c).

4. Conclusions

Aiming to exploit the high cycling stability and specific capacitance of noble metal-based materials, and the coupling with the stable and cheaper carbonaceous materials, very small osmium and ruthenium alloy NPs grown directly on the graphene surface were synthesized by one-step simple approach. To decouple the energy storage capacity from the power delivery rate, the synthesized nanostructure was tested as slurry electrodes in a flow energy system. The nanostructure showed excellent performance and stability over 200000 cycles. This electrochemical flow energy system can help to increase grid efficiency and assist implementation of renewable energy sources.

References

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Keywords
Energy storage; graphene; osmium-ruthenium alloy; flow energy system.