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## Enhancing the specific capacitance of SrRuO<sub>3</sub> and reduced graphene oxide in NaNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and KOH electrolytes

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### ABSTRACT

The specific capacitance (Cs), cycling stability, energy and power densities of SrRuO<sub>3</sub> (SRO) have been enhanced by reduced graphene oxide (RGO) in the form of SrRuO<sub>3</sub>-RGO (SRGO) composites. The high conductivity as well as the large specific surface area of RGO result in an improvement of the electrochemical and capacitive properties of SRO. The combination between RGO and SRO helps minimizing the mass percentage of Ru to 20.4% compared to 60% in RuO<sub>2</sub> and 43% in the individual SRO of commercial Ru-based supercapacitors. The electrochemical properties of RGO, SRO and SRGO were studied in three different electrolytes (1.0 M NaNO<sub>3</sub>, 1.0 M H<sub>3</sub>PO<sub>4</sub> and 1.0 M KOH), in which these materials are known to possess their optimum capacitances. We have found that RGO improves the Cs of SRO: from 13.8 F g<sup>-1</sup> to 62.4 F g<sup>-1</sup> in 1.0 M NaNO<sub>3</sub>, from 24.5 F g<sup>-1</sup> to 101 F g<sup>-1</sup> in 1.0 M H<sub>3</sub>PO<sub>4</sub> and from 52.4 F g<sup>-1</sup> to 160 F g<sup>-1</sup> in 1.0 M KOH, respectively. Moreover, it improves the cycling stability of SRO in all the studied electrolytes. In this study, we have found that 1.0 M H<sub>3</sub>PO<sub>4</sub> is suitable for high energy density applications, while KOH results in a supercapacitor of high maximum power density.

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### 1. Introduction

Nowadays, the developments in the field of green energy rely on finding sustainable and renewable energy resources rather than fossil fuels [1]. However, one of the greatest challenges is to store the electricity in a way that achieves both high power and energy densities [2].

Electric double layer capacitors (EDLCs), that can store charge by accumulation at the interface between the electrode surface and the electrolyte, are promising energy storage devices [3]. In contrast, devices in which the capacitance arises from a faradaic charge transfer between the electrode material and the electrolyte are called pseudocapacitors. Both pseudocapacitors and EDLCs are known as supercapacitors due to their high specific capacitances compared to the conventional capacitors. Pseudocapacitance

usually arises from metal oxides or polymeric materials while carbon materials are usually associated with an electric double layer capacitance. Meanwhile, supercapacitors provide many advantages over secondary batteries. They offer faster charge/discharge rates, higher cycling stability, and higher power density compared to Li-ion batteries [4]. So, the development of supercapacitors is very important, especially for high power applications. The combination of EDLCs with pseudocapacitors greatly improves the capacitance and provides high energy and power densities [5].

RuO<sub>2</sub> is one of the most promising materials for supercapacitor applications due to its high specific capacitance from 1300 to 2200 F g<sup>-1</sup> [6,7], high thermal stability, highly reversible faradaic reaction and high rate capability [8]. However, the high cost of RuO<sub>2</sub>, poor porosity, less cycling stability and rapid decrease of power density at high charge/discharge rates limits their commercial use [9]. One way to minimize the costs is the use of Ru in a perovskite structure. Here, Wilde et al. [10] stated that the inclusion of Ru in a perovskite structure leads to a decrease in the weight density of Ru from 60% in RuO<sub>2</sub>·nH<sub>2</sub>O to 43% in SrRuO<sub>3</sub>.

Perovskite is the name usually given to the general formula ABO<sub>3</sub>, where A is the larger cation, rare-earth metal or an alkali metal and B is the smaller cation such as transition metals [11].

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Perovskitic materials have attracted great interest due to their catalytic, electronic, optical, magnetic and ferroelectric properties [12–15] as well as their high-temperature sustainability and its significant role in fuel and solar cell applications [16,17]. The unique property of perovskites is their versatility in both chemical compositions and structural flexibility. Various combinations of A and B metals are possible such as  $A^+B^{5+}O_3$ ,  $A^{2+}B^{4+}O_3$ , and  $A^{3+}B^{3+}O_3$ . The structure can also accommodate smaller A-site cations and ranges of B–O–B bond angles that bring the oxide ions closer to the A-sites. These variations lead to some extent of distortion in the perovskite structure. Of course, using smaller B-site cations as well leads to further distortions [18].

Wilde et al. [10] studied the capacitive behavior of undoped SrRuO<sub>3</sub> as well as La or Mn-doped SrRuO<sub>3</sub> as efficient supercapacitor electrodes. They found that the maximum specific capacitance obtained for undoped SrRuO<sub>3</sub> was 10 F g<sup>-1</sup> and reaches 20–30 F g<sup>-1</sup> upon doping.

Other perovskitic materials have been studied by Wang et al. [18]. They studied the electrochemical behavior of LaMnO<sub>3</sub> and its doped form, La<sub>0.85</sub>Sr<sub>0.15</sub>MnO<sub>3</sub> that was prepared by the sol-gel method in 1.0 M KOH. At a current density of 0.5 A g<sup>-1</sup> the calculated specific capacitances of La<sub>0.85</sub>Sr<sub>0.15</sub>MnO<sub>3</sub> and LaMnO<sub>3</sub> were found to be 198 F g<sup>-1</sup> and 187 F g<sup>-1</sup>, respectively. Recently, N. Arjun et al. studied the pseudocapacitive behavior of La-based perovskites in 3 M LiOH solutions [19]. They found that LaNiO<sub>3</sub> shows the highest specific capacitance compared to the other perovskite structures, where the maximum Cs of LaNiO<sub>3</sub> was 106.58 F g<sup>-1</sup> compared to 16.43 F g<sup>-1</sup> for LaFeO<sub>3</sub>, 24.40 F g<sup>-1</sup> for LaCrO<sub>3</sub> and 56.78 F g<sup>-1</sup> for LaMnO<sub>3</sub> [19].

In the present work, we aimed to enhance the specific capacitance of SrRuO<sub>3</sub> by mixing it with highly conductive graphene sheets and to study the capacitive behavior of the resulting SrRuO<sub>3</sub>-RGO (SRGO) material. By varying the mass ratios between SrRuO<sub>3</sub> and RGO as well as the nature of the electrolytes, we optimized the system as well as the experimental conditions in order to harvest the maximum specific capacitance and cycling stability of the SRGO composite material.

## 2. Experimental

### 2.1. Preparation of SrRuO<sub>3</sub> using citrate method

The preparation of SrRuO<sub>3</sub> was carried out following the procedure mentioned in Ref. [20] based on a microwave-assisted citrate method. Briefly, 0.33 mmol of both Sr(NO<sub>3</sub>)<sub>3</sub> and RuCl<sub>3</sub>·xH<sub>2</sub>O were dissolved in 10 mL distilled water. The mixture was then ultrasonicated till complete solubility was reached. Then 0.66 mmol of citric acid was added so that the molar ratio between citric acid and total metal nitrates becomes 1:1. The mixture was sonicated again until homogeneity followed by adjusting the pH to 8.0 using NH<sub>4</sub>OH solution. The mixture was subjected to microwave irradiation using a power of 700 W for 30 min (the power was switched on and off for 20 s and 10 s, alternatively). The precursor was initially dehydrated and became viscous with time and finally the ignition process occurred. The as-resulted fluffy powder was grinded and transferred into a ceramic crucible prior to calcination at 600 °C for 3 h in an oven.

### 2.2. Preparation of reduced graphene oxide (RGO)

Graphene oxide was prepared by the modified Hummer method following the same procedure as reported previously [21]. Briefly, 5 g of high purity graphite was cured with H<sub>2</sub>SO<sub>4</sub>, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to prepare pre-oxidized graphite. This was followed by stirring 5 g of dried pre-oxidized graphite with 115 mL of concentrated H<sub>2</sub>SO<sub>4</sub>

in an ice bath for about 10 min. Then 15 g of KMnO<sub>4</sub> was gradually added and stirring was continued for two more hours. The mixture acquired a bright yellow color after its dilution by water and treatment with H<sub>2</sub>O<sub>2</sub>. The bright yellow suspension was filtered and washed with 1:10 HCl solution then it was dried overnight in an oven at 80 °C. RGO was prepared as mentioned in Ref. [22]. Briefly, 0.1 g of GO was dissolved in 20 mL of deionized water and ultrasonicated for 2 h. The suspension was centrifuged to get rid of the unoxidized GO before adding 150 μL of hydrazine hydrate (HH). The microwave oven was used to reduce GO into RGO by its operation with a power of 900 Watt for 30 s cycles (the power was switched on and off for 20 s and 10 s, alternatively) for four cycles. The resulted black RGO sheets were filtered, washed and dried.

### 2.3. Preparation of the SrRuO<sub>3</sub>-RGO mixture (SRGO)

A 10 mg/mL suspension of SRGO was prepared by mixing SrRuO<sub>3</sub> with RGO in various mass percentages (from 25 to 80% w/w) and dissolved in dimethyl formamide (DMF). The suspension was ultrasonicated for an hour until a homogeneous suspension was obtained. For comparison, 10 mg/mL of pure SrRuO<sub>3</sub> and RGO suspensions were prepared by the same way.

### 2.4. Structural, spectral and surface analysis

The resulting samples were characterized using Raman spectroscopy, field-emission scanning electron microscope (FESEM) with energy dispersive X-ray (EDX) analysis and high-resolution transmission electron microscopy (HR-TEM). The Raman spectra were obtained using a Witec alpha 300R confocal Raman microscope with a 532 nm Nd:Yag laser. The surface morphological analysis was performed using HR-TEM (Tecnai G20, FEI, Netherland, 200 kV, LaB<sub>6</sub> Gun), FESEM and EDX were measured using JEOL JSM-6360LA and Philips XL30.

### 2.5. Electrode fabrication and electrochemical measurements

A 10 μL of 1% Nafion solution was added to the surface of well-polished and mirror-like Ni electrode (99.5% Ni rod from Johnson Matthey Inc. with a surface area of 0.283 cm<sup>2</sup>) and dried at 80 °C. Afterwards 20 μL of the active material was immobilized on the surface of Ni/Nafion and left to dry in an oven to obtain Ni/N/RGO, Ni/N/SRO, Ni/N/SRGO. The masses of active materials were found to be 0.2 mg while the surface area of Ni electrode is 0.283 cm<sup>2</sup>. The electrochemical measurements were performed in a conventional three-electrode system using Ag/AgCl (4 M KCl) as a reference electrode and Pt wire as a counter electrode. The used electrolytes were 1.0 M NaNO<sub>3</sub>, 1.0 M KOH and 1.0 M H<sub>3</sub>PO<sub>4</sub>. Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS) experiments were performed using a Voltalab PGZ301 potentiostat. Cyclic voltammetry curves were recorded with different potential windows based on the used electrolytes (from 0.0 V to 1.0 V for 1.0 M NaNO<sub>3</sub>, from -1.0 V to 0.2 V for 1.0 M KOH and from -0.2 V to 1.0 V for 1.0 M H<sub>3</sub>PO<sub>4</sub>). The effect of scan rate was studied in the range from 2 mV/s to 200 mV/s. Galvanostatic charging/discharging curves were recorded using chronopotentiometry at various current densities (from 1 to 25 A. g<sup>-1</sup>). The specific capacitance was calculated from the cyclic voltammograms by using eq. (1) and from galvanostatic charging/discharging curves using Eq. (2), where Cs is the specific capacitance in Farad per gram,  $\bar{I}$  is the integration of area enveloped inside the CVs,  $m$  is the mass of electroactive material in grams,  $\Delta V$  is the potential window in Volts ( $V_f - V_i$ ),  $I$  is the current in Ampere and  $t_d$  is the discharge time in seconds.

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