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Pseudocapacitive rare earth gallium oxides (RE_3GaO_6): A potential electrode family for asymmetric supercapacitors

Bagavathy Shunmughananthan [a], Ramesh Rajendran [b], Balaji Krishnasamy [c], Moorthy Babu Sridharan [d], Thangaraju Dheivasigamani [a,*]

[a] Nano-crystal Design and Application Lab (n-DAL), Department of Physics, PSG Institute of Technology and Applied Research, Coimbatore, Tamil Nadu 641062, India
[b] Department of Physics, Periyar University, Salem, Tamil Nadu 636011, India
[c] Department of Chemistry, PSG Institute of Technology and Applied Research, Coimbatore, Tamil Nadu 641062, India
[d] Crystal Growth Centre, Anna University, Chennai, Tamil Nadu 600025, India

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ABSTRACT

The shortcomings of existing energy storage devices have prompted an increased interest in exploring supercapacitor devices and novel electrode materials. Integrating rare earth elements (REE) with gallium oxides as the host material might be a promising approach for enhancing supercapacitor performance. This work employs an effective gel matrix route to synthesize rare earth gallium oxides, specifically RE_3GaO_6 (RE = Eu, Gd, Dy, and Er). The crystallinity, phase purity, optical properties, chemical composition, and morphology of the materials were identified using various characterizations, including XRD, Raman, UV, XPS, and SEM. Electrochemical measures such as CV, GCD, and EIS suggest that the Eu_3GaO_6-based electrode shows a higher capacitance of 774 F g^{-1} (552.8 F cm^{-3}) at 1 Ag^{-1} amidst the synthesized rare earth gallium oxides. Asymmetric supercapacitor electrodes were fabricated using well-performed material and have been studied. The energy and power density of asymmetric supercapacitors are about 33.9 $Whkg^{-1}$ (13.5 Wh L^{-1}) and 750 W kg^{-1} (300 W L^{-1}), respectively, with a retention efficiency of 80.8 %.

1. Introduction

The rapid industrialization, technological advancement, and depletion of fossil fuel resources have led to a demand for energy. The most efficient and useful systems for electrochemical storage and energy conversion are supercapacitors, a potential energy storage candidate. Supercapacitors (SC) possess high-power density, long lifespan, and quick charge discharging rate, which unite the advantages of batteries and conventional capacitors that have been at the forefront of research [1]. They have been widely studied in medical devices, military, aerospace, and portable consumer electronics, and larger-scale industrial power systems [2]. The electrochemical reaction on the material's surface remains the basis of energy storage for supercapacitors. These reactions include the combination of faradaic chemical reactions (pseudo capacitor) and accumulation/separation (EDLC) processes [3]. The pesudocapacitors allow charges to be retained and promote a quick, reversible faradaic process, thereby raising the energy density over that of EDLCs [4]. Also, pesudocapacitors possess 10–1000 times higher capacitance values than EDLCs [5]. However, their commercial application is limited due to their lower energy density. Therefore, boosting their energy density remains an efficient approach to tackle future energy needs without impacting cycle life and power density [6]. The energy density (E) is:

$$E = \frac{1}{2} C \times V^2 \tag{1}$$

According to Eq. (1), the working voltage (V) and the specific capacitance (C) help in extending the energy density of a supercapacitor [7]. Furthermore, the capacitance relies on the active electrode materials with desirable characteristics such as high electrical conductivity, electrochemically active sites, high chemical and thermal stability, significant surface area, pore size, and organized structure that can be adjusted [8]. These features prompted the scientific community to do an enormous study on electrode materials, including hydroxides, phosphides, sulphides [9], metal-organic frameworks [10], and TMOs, as well as their composites, in order to meet the demands for developing supercapacitors with extremely high power, energy density and capacitance [11–13]. Selecting electrode materials with exceptional

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* Corresponding author.
E-mail address: dthangaraju@gmail.com (T. Dheivasigamani).

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electrochemical stability, power density, and power is crucial [14].

Gallium oxide-based nanomaterials with unique properties find many applications in gas sensors, photocatalysis, optoelectronic devices, and drug carriers [15]. Gallium-related materials have gained interest in energy storage in recent years because of their superior electrochemical performance. They have been the subject of recent and future investigations because of their many excellent properties, including fast charge-discharge rates, excellent electron mobility, increased power density, long life, remarkable physiochemical stability, and the ability to apply high voltages. Their unique properties render them an excellent choice for electrode materials in supercapacitors [16].

Rare earth-based nanomaterials are gaining interest and finding a vast range of applications mainly because of their peculiar unpaired 4 f electronic configuration and remarkable chemical and physical attributes [17]. Because of their unique magnetic, electric, and optical properties, rare earth elements are utilized in various potential applications, including fuel cells, the glass industry, and catalysis [18]. The rare earth elements are characterized by their large ionic radii, low electronegativity, and strong affinity for oxygen. These properties, combined with their common redox couples of $3^+/2^+$ or $4^+/3^+$, make them highly suitable for various electrochemical processes, enhancing their efficiency and versatility in energy storage and conversion applications [19]. These compounds exhibit remarkable potential for electrochemical energy storage due to their superior ionic conductivity and outstanding mechanical properties [20]. Also, nanocrystalline rare earth element's enhanced surface-to-volume ratio provides more active sites for electrochemical reactions. This enhanced surface area boosts reaction efficiency, making these materials highly effective for applications in energy storage, conversion, and other electrochemical processes [21]. In addition, they have favorable conductivity and redox properties, making them suitable for pseudo capacitors. Additionally, they have high bulk density, which might help achieve higher effective capacitance [4].

Numerous studies have explored RE-based materials and their nanocomposite as electrodes in improved energy storage devices [22]. Kalai Chalvan et al. employed a green-mediated route for synthesizing Dy $^{3+}$ doped $AgGaO_2$ nanoparticles using the gel extracted from Aloe vera, studied photoluminescence properties, and examined their suitability for supercapacitor application. The dependence on dopant concentration is highlighted by the resultant variations in morphology and the supercapacitance values, which range from 76.177 to 111.53 F/g [23]. Aydin et al. fabricated a CNF/Gd_2O_3 electrode, which exhibited a specific capacitance of about 162.3 F g^{-1} and an energy density of about 8.12 Wh kg^{-1} [24].

Few researchers have explored and compiled the rare earth metal oxides for energy storage applications. Schneider et al. and Nicolas et al. reported $RE_3Ga_5O_{12}$, RE_3GaO_3, RE_3GaO_6, and $RE_4Ga_2O_9$ as the four distinctive compounds that exist in rare earth oxides and Ga_2O_3 pseudo-binary systems [25,26], which have been extensively investigated for their optical and magnetic properties [27]. Commonly studied YAG and available aluminium garnets possess a dielectric nature and find many applications in phosphors, bioimaging, and lasers. As garnets possess huge unit cell volume and enhanced refractive index, substituting aluminium with gallium atoms will improve their performance. Thus, the replacement of gallium in the aluminium site results in a semiconducting nature. Rare reports on integrating the structures of rare earth gallium oxides for energy storage applications lead to curiosity about these materials. Recent investigations on rare earth gallium garnet and its other phases, including $RE_3Ga_5O_{12}$ (RE= Sm, Gd, Dy, Eu, Er, Yb, and Lu), Sm_3GaO_6, $Pr_4Ga_2O_9$ report the performance of energy storage applications [28–32]. Implementing rare earth gallium-based electrode materials could be the new era in supercapacitor applications.

This study investigates the application of rare earth gallium oxides in energy storage applications, specifically RE_3GaO_6 (where RE = Eu, Gd, Dy, Er). Four different rare earth gallium oxides were successfully synthesized employing a facile gel-matrix approach, providing a cost-effective and efficient route for obtaining single-phase rare earth gallium oxides. Various characterization analysis of RE_3GaO_6 was carried out to understand their structural, morphological, and other properties. The supercapacitor performance of these rare earth gallium oxides was investigated, which provided insights into their capacitance, charge-discharge behavior, and electrochemical stability. The used english abbreviation in the article is tabulated in Table 1.

2. Experimental method

2.1. Materials

Gallium trichloride ($GaCl_3$) of 98 % purity was procured from Tokyo Chemicals. Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$, 99.7 % purity) from SISCO Labs and Ethane-1,2-diol ($C_6H_6O_2$, 99 %) from HiMedia were used without purification. All rare-earth nitrates used in this investigation are prepared from respective rare-earth oxides (99.9 %) using nitric acid.

2.2. Synthesis

A cost-effective gel matrix route synthesizes a series of rare-earth gallium oxides RE_3GaO_6 (RE = Eu, Gd, Dy, and Er). 1.5 mmole of rare earth nitrate (RE = Eu, Gd, Dy, and Er) is added to 30 mL of distilled water, and 0.5 mmole of $GaCl_3$ is mixed in deionized water (20 mL) and stirred separately for total dissolution of the precursors. Then, the prepared solutions are mixed, and 2 mmole of $C_6H_8O_7{\cdot}H_2O$ is added. The resultant solution is then heated with constant stirring. At 70 °C, $C_6H_6O_2$ (binder) is added in drops to the solution for complex formation. The temperature of about 80 °C is maintained with constant stirring throughout the experiment until the gel formation. The procured gel is pretreated at 250 °C and annealed at 950 °C for 2h. The resultant product is collected and used for further analysis.

2.3. Characterization

The phase purity of prepared particles was analyzed using Powder X-ray Diffraction XPERT PANlytical using Cu Kα radiation. Horiba Jobin Yuvon 800 Raman spectrometer was used to investigate the vibrational and spectral characteristics of the material. The optical properties of RE_3GaO_6 particles are examined using a Thermofisher UV–visible spectrophotometer. The prepared material's oxidation state and chemical constituents are studied from XPS using Thermo Scientific K – Alpha Surface analysis with Al source. The morphology of prepared particles is analyzed using ZEISS Sigma Field Emission Scanning microscopy (FESEM). Elemental mapping of the synthesized materials is examined using Nano XFlash Detector, BRUKER. Admiral Instruments - Squidstat Plus is used to conduct electrochemical analysis of the material.

2.4. Electrochemical measurement

A mixture of 85 % synthesized active material, 10 % activated carbon, and 5 % PVDF (Polyvinylidene fluoride) was prepared for electrode

Table 1
Abbreviations.

REE	Rare Earth Elements
EDLC	Electric Double Layer Capacitor
TMOs	Transition Metal Oxides
CIF	Crystallographic Information File
XRD	X-Ray Diffractometry
XPS	X-ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
CV	Cyclic Voltammetry
GCD	Galvanostatic Charge Discharge
EIS	Electrochemical Impedance Spectroscopy
ASC	Asymmetric Supercapacitor