

Robust cyclic stability and high-power performance of Ni/Mg co-doped CeO₂ electrodes for asymmetric hybrid supercapacitors

Muddasira Sarwar^a, Muhammad Shahbaz^b, Rabia Ghaffar^c, Mohsin Saleem^{d,g,**},
Muhammad Zubair Khan^{e,***}, Muneeb Irshad^f, Shahzad Sharif^b, Jung Hyuk Koh^{g,****},
Muhammad Haseeb^a, Abdul Ghaffar^{a,*}, Imran Shakir^h, Kamran Aliⁱ

^a Department of Physics, Government College University, Lahore, 54000, Pakistan

^b Materials Chemistry Laboratory, Institute of Chemical Sciences, Government College University, Lahore, 54000, Pakistan

^c Division of Science and Technology, Department of Botany, University of Education, Lahore, 54000, Pakistan

^d School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), H-12, Islamabad, 44000, Pakistan

^e Pak-Austria Fachhochschule: Institute of Applied Sciences, Department of Materials Science and Engineering, Haripur, KPK, Pakistan

^f Department of Physics, University of Engineering and Technology, Lahore, 54890, Pakistan

^g School of Electrical and Electronic Engineering, Chung-Ang University, Seoul, Republic of Korea

^h Department of Physics, Faculty of Science, Islamic University of Madinah, Madinah, 42351, Saudi Arabia

ⁱ Faculty of Integrated Technologies, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong, BE, 1410, Brunei Darussalam

ARTICLE INFO

Keywords:

Ceria
Ni
Mg as dopants
Solution combustion synthesis
Electrochemical measurements
High-power supercapacitor

ABSTRACT

Ceria co-doped with Ni and Mg (Ni, Mg@CeO₂) was examined for its electrochemical performance, showing impressive power density and cyclic stability in the fabricated device. The material was synthesized using an easy, low-cost solution combustion method. Two different materials were studied to evaluate the impact of co-doping: pristine CeO₂/AC (M – 1) and Ni, Mg@CeO₂ composite with AC (Activated Carbon) (M – 2). Structural analysis confirmed the face-centered cubic (FCC) structure of CeO₂ through X-ray diffractometry (XRD). The structural and optical properties were characterized by using field-emission scanning electron microscopy (FESEM) and photoluminescence (PL) spectroscopy, respectively. The electrochemical behavior was tested with cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), revealing the pseudocapacitive nature of the ceria-based electrodes. As an electrode material, CeO₂/AC (M – 1) achieved a higher specific capacitance (C_s) of 244.4 F/g at 0.5 A/g, while Ni, Mg@CeO₂/AC (M – 2) showed 197.6 F/g at the same current. In a full-device setup, Ni, Mg@CeO₂/AC (M – 2) reached a C_s of 63.3 F/g at 0.5 A/g, along with excellent cycling stability, retaining 100.4 % coulombic efficiency over 5000 GCD cycles. The hybrid device based on Ni, Mg@CeO₂/AC displayed a maximum specific energy of 18.3 Wh/kg and a specific power of 467.5 W/kg at 0.5 A/g.

1. Introduction

The development of sustainable, non-polluting renewable energy systems and advanced energy storage technologies is critical, as fossil fuels, our primary energy source, may be depleted within decades [1,2]. Depleting reserves, along with growing climatic and environmental

concerns, have compelled us to reevaluate traditional energy generation methods and seek viable alternatives [3]. The transition to renewable energy has increased the demand for efficient and reliable energy storage solutions. As non-renewable resources diminish, attention has shifted to enhancing energy storage devices [4,5]. Among available energy storage technologies, supercapacitors and batteries offer distinct

* Corresponding author.

** Corresponding author. School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), H-12, Islamabad, 44000, Pakistan

*** Corresponding author.

**** Corresponding author.

E-mail addresses: mohsin852@cau.ac.kr (M. Saleem), zubair.khan@fcm3.paf-iast.edu.pk (M. Zubair Khan), jhkoh@cau.ac.kr (J.H. Koh), abdulghaffar@gcu.edu.pk (A. Ghaffar).

<https://doi.org/10.1016/j.mtsust.2025.101272>

Received 12 October 2025; Received in revised form 19 November 2025; Accepted 8 December 2025

Available online 9 December 2025

2589-2347/© 2025 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

advantages and limitations, making their optimization and integration essential for a sustainable energy future [6,7]. Batteries offer high energy density, while supercapacitors provide high power density [8–10], prompting researchers to investigate hybrid systems that incorporate both advantages [11]. This has led to extensive studies on hybrid supercapacitor designs to address the limitations of conventional energy storage technologies [12].

Supercapacitors, also known as electrochemical capacitors, are a particular kind of energy storage device that has exceptional characteristics such as a long-life cycle, high specific power (up to 10 kW/kg), ultra-fast charging-discharging rate, and excellent reversibility [13,14]. Metal oxides and conductive polymers are also being considered as electrode materials due to their pseudo-capacitance nature that is based on the underlying redox reaction [15]. Cerium oxide has been studied extensively in composite forms [16] and as a co-doped material [17]. Cerium oxide doped with Cr atoms exhibits a C_s of 42.6 F/g at 5 mV/s [18]. The effects of electrolytes, including NaCl, KCl, Na_2SO_4 , and K_2SO_4 , have been investigated using ceria as the electrode material. A maximum C_s of 523 F/g at a 2 mV/s rate has been found for NaCl with 82 % retention after 2000 cycles [19].

Cerium oxide-based electrode materials are famous due to their resistance to corrosion, notable physical and chemical properties, and durability in both chemical and biological environments [20]. The conducting polymers have also been used for electric energy storage purposes [21]. Carbon-based materials like graphene/ CeO_2 , Co_3O_4 /graphene, and metal/Au nanoparticles exhibit elevated specific capacitance, making them valuable choices for electrode materials. In EDLC capacitors, the storage of energy arises from the gathering of charges at the interfacial region between electrode material and electrolyte, whereas in redox capacitors, a battery-like oxidation-reduction reaction takes place. The electrode materials frequently utilized in pseudo capacitors consist of metal oxides such as RuO_2 [22], Co_3O_4 [23], MoO_2 [24], MnO_2 [25], and NiO [26].

Porous CeO_2 synthesized through combustion achieves a $C_s=134.6$ F/g and retains 92.5 % cyclic stability after 1000 cycles at 1 A/g [27]. Employing the hydrothermal route, hexagonal nanoplates of ceria have been produced that exhibited the highest C_s of 644 F/g at 0.5 A/g [28]. The super capacitive performance of Ni-doped CeO_2 was evaluated, revealing specific capacitances of 235 F/g (pure CeO_2), 351 F/g (1 % Ni-doped), 382 F/g (3 % Ni-doped), 577 F/g (5 % Ni-doped), and 417 F/g (7 % Ni-doped) at a 2 A/g rate [29]. Ni-doped ceria nanospheres combined with polyaniline revealed remarkably a $C_s=866$ F/g at 1 A/g and energy density of 120.3 Wh/kg [30]. Mg-doped CeO_2 demonstrates a C_s of 130 F/g at 1 A/g [31]. In contrast, Ag-decorated CeO_2 /reduced graphene oxide (rGO) composites show a significantly higher C_s of 710.42 F/g at 0.2 A/g [32]. Ceria quantum dots doped with Ni-Co hydroxide nanosheets yield an exceptional C_s of 1370.7 F/g at 1 A/g with 90.6 % retention after 4000 cycles [33].

Ceria, in combination with other materials [34], has also been studied for use as an electrode of a supercapacitor. It has been reported that the $\text{Ce}_{1-x}\text{Ni}_x\text{O}_2$ ($x=0.1$), developed by the combustion method, shows a specific capacitance of 446 F/g with 96.1 % stability after 2000 GCD cycles [35]. CeO_2 and NiO in composite form have revealed specific capacitance and energy densities of 8.418 mF/g and $1.052 \text{ mF/g} \times \text{v}^2$, respectively [36]. Due to the synergistic redox nature and conducting behavior, CeO_2 /CNTs showed a C_s of 818 F/g at 1 mV/s [37]. In a similar case, where instead of CNT-activated carbon has been used, a composite of CeO_2 /AC displays $C_s=162$ F/g [38]. **The graphitic carbon-coated hollow CeO_2 spheres (H- CeO_2 @GC) exhibit a surface area of $153 \text{ m}^2/\text{g}$ and enhanced electrochemical behavior, including a notable $C_s=501$ F/g at 1 A/g [39].** Modification of the electrolyte also affects supercapacitive performance. For example, adding 0.2 M of $\text{K}_4[\text{Fe}(\text{CN})_6]$ as a redox additive to 3 M KOH electrolyte enhances the electrode ZnO/ CeO_2 nature. The maximum specific capacitance is 1069 F/g at 5 mV/s with a maximum energy density of 39.6 Wh/kg at 3A/g [40]. There is already much work done on ceria in

different conditions and combinations. After a careful survey, it has been found that the co-doping of Ni and Mg in the cerium oxide has not yet been studied.

Doping of more than one element or multimetal/nonmetal alloys can lead to effects different from the host material. The co-doped ceria has shown better features as compared with the ceria with one metal [41]. Theoretically based on DFT, the co-doping of In^{3+} , Sm^{3+} in CeO_2 showed that the ionic conductivity as a function of local structures [42]. The system of $\text{Ce}_{0.78}\text{Fe}_{0.02}\text{Cu}_{0.20}\text{O}_2$ was synthesized via the co-precipitation approach, revealing saturation magnetization of $1.3 \times 10^{-2} \text{ emu/g}$ [17]. In other systems, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ as a multielement-doped electrode material exhibits excellent 76 J/cm^3 energy density [43]. Also, $\text{Ge}_{0.59}\text{Au}_{0.02}\text{Ag}_{0.11}\text{Sb}_{0.13}\text{Pb}_{0.12}\text{Bi}_{0.01}\text{Te}$ as a thermoelectric system showed a thermal conductivity of 0.22 W/mK and $zT=2.0$ at 780 K [44]. A $\text{NaNi}_{0.40}\text{Mn}_{0.40}\text{Ti}_{0.13}\text{Fe}_{0.06}\text{Al}_{0.01}\text{O}_2$ (NaNMTFA) is a complex alloy developed for the solid-solution reactions for large voltage window [45]. As same above, LiFePO_4 is famous for the cathode in battery configuration due to physical and chemical stability and long lifespan [46]. Conductive MOF combined with MXene as an electrode has shown super capacitive performance as of 416.6 F/g at 0.5 A/g [47]. Similarly, the conductive MOF when introduced to the Ni, NiCo and Co etc. revealed there outstanding super capacitive performance and stability [48]. In short, metal or metal oxides along with the doped elements inspire new features of base materials for certain applications. Therefore, it is strongly expected that the co-doping of Ni and Mg affect the ceria in terms of its physical and chemical properties.

Already, pristine CeO_2 has been studied in literature very well. In this study, the solution combustion approach is utilized to synthesize highly porous Ni,Mg co-doped cerium oxide nanostructures for supercapacitor electrodes. It is observed that porous ceria (CeO_2) with spherical morphology has better retention and maximum energy density when co-doped with Ni and Mg and is further considered as a composite with activated carbon.

2. Synthesis of electrode material

Precursors of purity >99 % were bought from Sigma-Aldrich and used to synthesize the desired electrode materials based on the exothermic redox reaction involved in the solution combustion synthesis.

2.1. Electrode material M – 1 (CeO_2 with activated carbon)

$(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ was dissolved in 50 mL deionized water (DIW) and heated at 90°C for a few minutes. Separately, the activated carbon in 20 mL of DIW was heated at 90°C , and then the prepared suspension was added to $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ solution. At this stage, oxalic acid was added to the earlier solution and further heated at 90°C . The DIW evaporated, leading to a gel-like material after 3 h. At the end of the combustion process, ignition, burning, and production of fumes, all these processes were noticed. Eventually, the powder was left that was heated at 400°C for 2 h in open air to achieve FCC CeO_2 . The obtained material was crushed to produce a refined powder.

2.2. Electrode material M – 2 (Ni, Mg@ CeO_2)

To prepare 5 wt% Ni and 5 wt% Mg co-doped CeO_2 material, certain amounts of Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Mg $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors were dissolved in 20 mL DIW independently and heated for a few min. A host solution was prepared by 90 wt% $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ into 50 mL DIW and heated at 90°C . Both Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Mg $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions were poured into the host solution simultaneously and heated for a few minutes at 90°C . At this stage, after the addition of oxalic acid, the resultant mixture was kept at 90°C till the evaporation of water left a gel-like material. In the end, the powder was developed and was sintered at 400°C for 2 h to get the Ni, Mg@ CeO_2 phase.

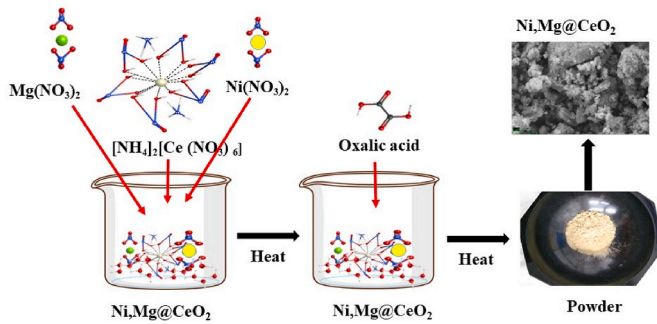


Fig. 1. A combustion-based synthesis scheme for Ni,Mg co-doped ceria (M – 2).

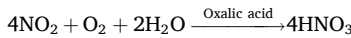
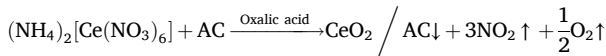
2.3. Electrode material M – 3 (Ni, Mg@CeO₂/AC)

In addition to the steps involved in the preparation of material M – 2, AC (Activated Carbon) was added to develop Ni, Mg@CeO₂/AC composite. Finally, sintering of the material was done at 400 °C for 2 h and pulverized using a mortar and pestle.

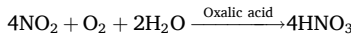
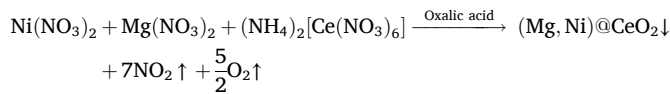
All three samples were sintered at 400 °C, relatively at low temperatures to attain low crystallinity in the end samples. This was considered to keep the agglomeration effect low to have large surface for the activation process during the charge storing process.

The underlying chemistry of the synthesis process is explained in the following equations and Fig. 1.

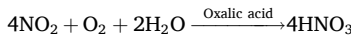
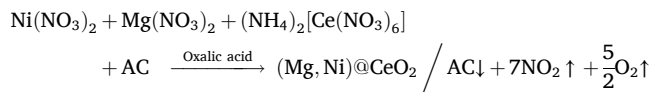
For CeO₂/AC



For Mg, Ni@CeO₂



For (Mg, Ni)@CeO₂/AC



2.4. Electrode development

A slurry was prepared for the fabrication of a working electrode by mixing M – 1 (active material), polyvinylidene fluoride (PVDF) binder, and activated carbon conducting agent (80/10/10) in N-methyl pyrrolidone (NMP) solvent. For homogenization, magnetic stirring was done overnight at 200 rpm. A piece of nickel foam measuring 1 × 1.5 cm² was cleaned by sonication in nitric acid, DIW, and ethanol, then drying was done in an oven for 3 h. The synthesized slurry was subsequently drop-cast onto the pretreated nickel foam and dried at 60 °C. The mass loading was 4 mg/cm². A similar procedure was followed for the fabrication of the M – 2 electrode. Moreover, for constructing a hybrid device, a slurry of activated carbon (AC) was prepared using the same composition, and Eq. (1) was utilized to balance the mass and charge of the two electrodes [49]. The mass of AC was calculated as 4 mg.

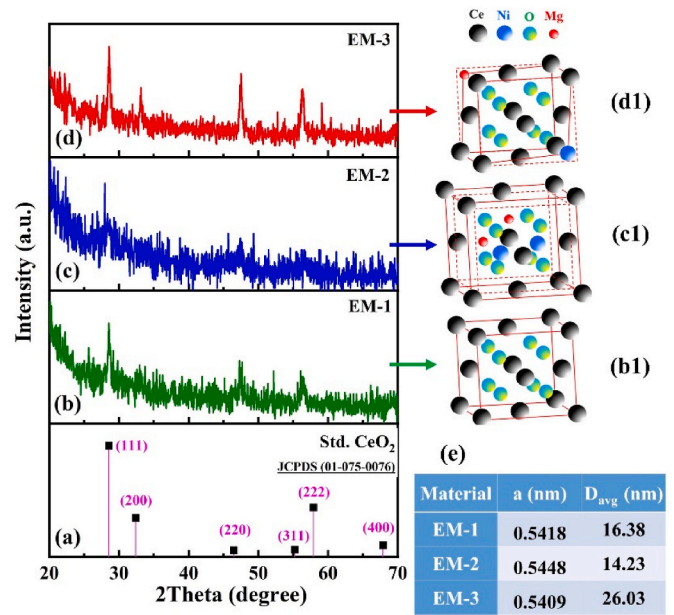


Fig. 2. XRD patterns and effect of co-doping. (a) Standard CeO₂ diffraction peaks according to JCPDS card, (b) Composite of CeO₂ with AC as M – 1, (c) co-doped CeO₂ with Ni and Mg as M – 2, (d) Composite of Ni and Mg co-doped CeO₂ and AC as M – 3, (b1) Lattice of CeO₂, (c1) Expansion of CeO₂ matrix due to Ni and Mg interstitial doping, (d1) Contraction of CeO₂ matrix due to Ni and Mg doping, i.e., substitutional doping, and (e) Lattice parameters.

$$\frac{m_+}{m_-} = \frac{C_s \times \Delta V_-}{C_s \times \Delta V_+} \quad \text{Eq 1}$$

Where m signifies mass, m₊ is the mass of the positive electrode and m₋ is the mass of the negative electrode, C_s represents specific capacitance, and ΔV is the potential window.

3. Characterizations

An X-ray diffractometer was used for the powder XRD measurements, which were performed using a CuK_α-1 X-ray source with a wavelength of 1.54056 nm. The infrared Fourier Transform spectra of the prepared samples were recorded using Shimadzu's IR Prestige-21, covering the wavenumber range of 4000–400 cm⁻¹. For the inelastic scattering measurements of photons by the materials, an I-Raman USA system was employed. The maximum operational power was 50 mW, with a 532 nm laser integrated into the Raman setup.

4. Results and discussion

4.1. X-ray diffraction analysis

The measured X-ray diffraction profiles of M – 1, M – 2, and M – 3 are presented in Fig. 2b–d. The diffraction peaks at 28.3°, 32.9°, 47.3°, 56.0°, 59.6°, 69.0°, and 76.7°, correspond (111), (200), (220), (311), (222), (400), and (331), respectively, indicating the face-centered cubic phase of CeO₂ with JCPDS card no. 01-075-0076 [38]. Peak shifting in the (111) peak is noticed for both M – 2 and M – 3 due to Ni and Mg co-doping in the Ce-O matrix, as sketched in Fig. 2b1-d1. The lattice parameter and crystallite size are given in Fig. 2e.

The fused hexagonal layered structure [50] of activated carbon (AC) provides a surface for the heterogeneous crystallization of the CeO₂. Due to the similar close-packed nature of the crystal structures of CeO₂ and AC, there is a favorable situation that CeO₂ adsorbs on the AC surface, leading to improved crystallinity (Fig. 2d) and spherical morphology of

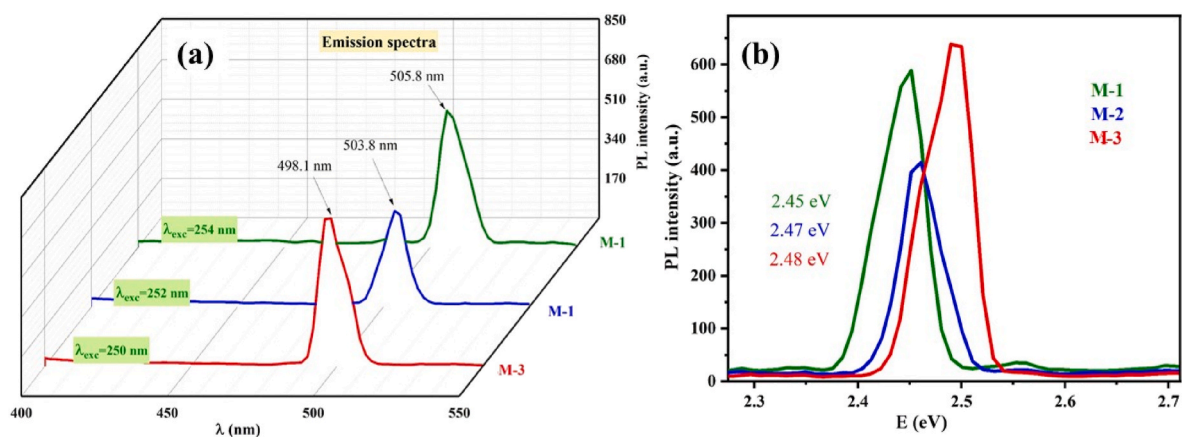


Fig. 3. PL spectra of Cerium oxide co-doped with Ni and Mg.

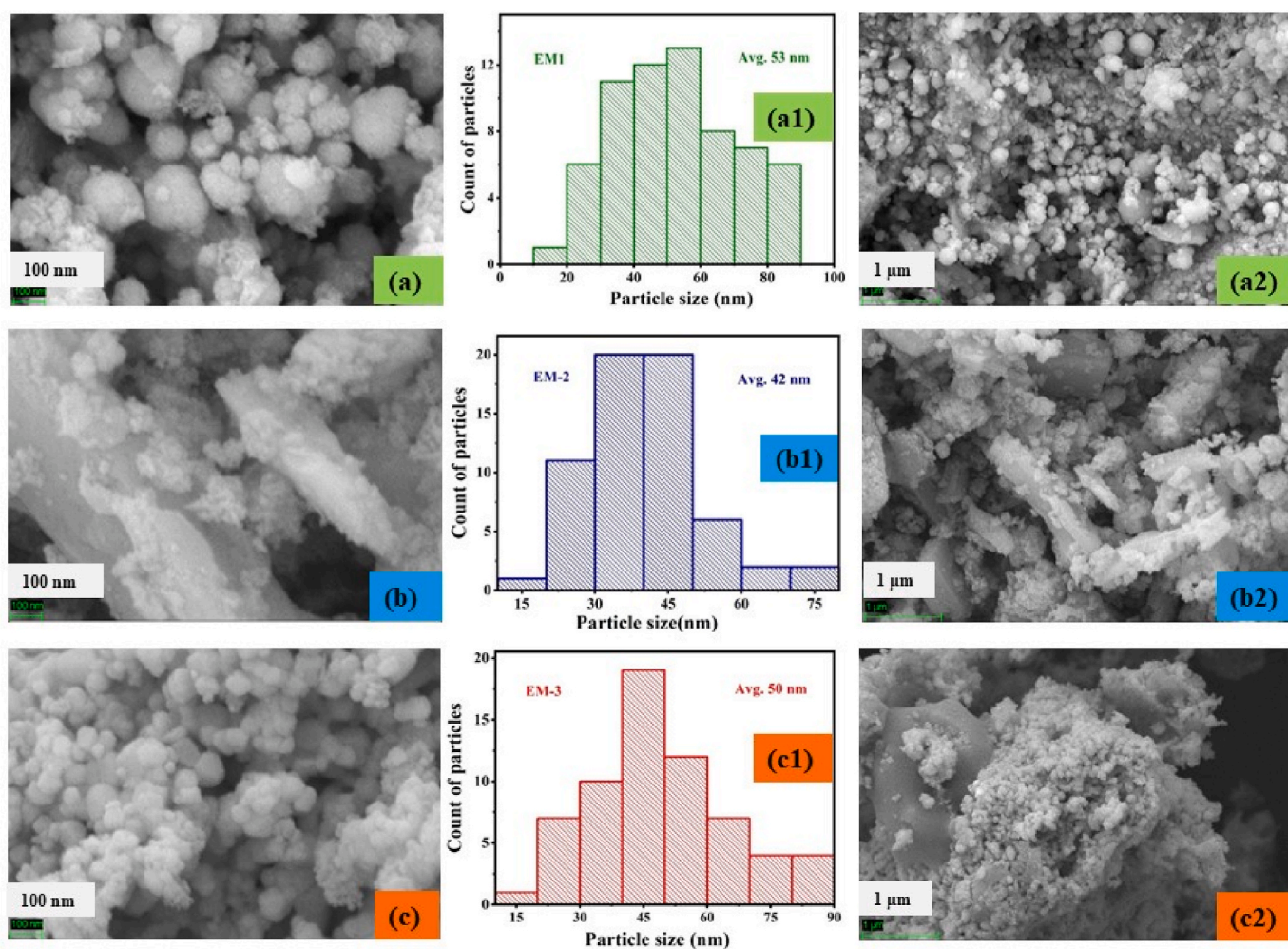


Fig. 4. FESEM images and particle size distributions of M-1 (a, a1, a2), M-2 (b, b1, b2) and M-3 (c, c1, c2). Visible particle size distributions (a1-c1) are obtained considering images at the scale of 100 nm.

the end particles (Cf. SEM images). Concerning doping, the possibilities are as follows. i) Ni and Mg are doped independently in the CeO_2 matrices, ii) Ni and Mg are doped together in the CeO_2 matrix, and iii) Ni and Mg are doped into the CeO_2 matrix via substitutional or interstitial modes. For Ni,Mg co-doped CeO_2 composite with AC, the doping of atoms seems to be interstitial, leading to an increase in the net volume of the unit cell (Fig. 2c1). Hence, the shifting of the peak to the left is seen

for M-2 and the increased lattice parameters. But, for M-3, being smaller in size of Ni and Mg as compared to the Ce, the volume of a doped unit cell is less than compared of the pristine (Fig. 2d1).

4.2. Photoluminescence spectroscopy

Fig. 3 shows the spectra of photoluminescence (PL) measurements of

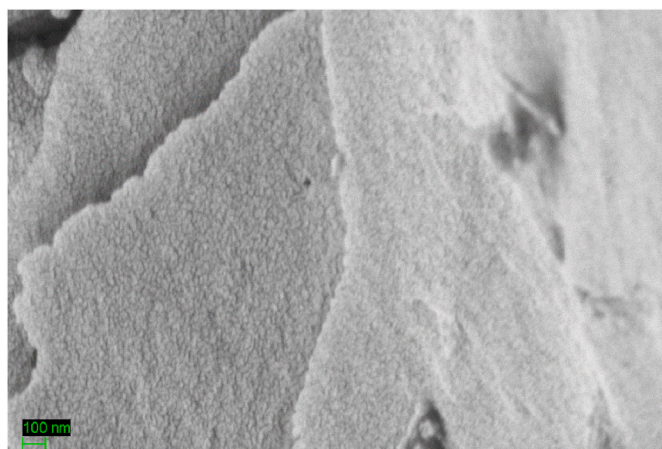


Fig. 5. FESEM image of Activated Carbon AC.

Ni, Mg co-doped CeO_2 for the range of 400–550 nm. For CeO_2 in M – 1, the PL emission peak is observed at 505.8 nm and the excitation peak at 254 nm. Similarly, for M – 2, the emission and excitation peaks are at 503.8 nm and 252 nm, respectively. Also, for M – 3, these are 498.1 nm and 250 nm as emission and excitation peaks, respectively. The PL spectra exhibit band gap energies of 2.45, 2.47, and 2.48 eV for M – 1, M – 2, and M – 3 that lie in the visible-blue region. Peak shift to a lower wavelength is due to Ni, Mg co-doping in the CeO_2 matrix [51]. The increasing particle size makes the recombination process weaker; consequently, the excitation process takes place at a reduced speed. The intensity of the spectra is higher for M – 1 and M – 3 due to the spherical symmetry, which means a lower number of defects. There is a red shift in the semi-intense PL spectra for three different CeO_2 -based materials showing the variations in the oxygen vacancies, crystallite boundaries and poor crystallinity (Cf. Fig. 2). The increasing particle size causes the recombination process to get weaker; consequently, the excitation process takes place at reduced speed [52].

4.3. FESEM analysis of electrode material

Based on the scanning electron micrographs, the morphology and size distribution of M – 1, sintered at 450 °C, is shown in Fig. 4a–a2. The average particle size of 53 nm (Fig. 4a1) is obtained for M – 1 using ImageJ software. Similarly, by applying ImageJ software, the average particle sizes of 43 nm and 50 nm are calculated for M2 (Fig. 4b1) and M3 (Fig. 4c1), respectively. Ceria particles in spherical shape are present in the FESEM images. The spherical appearance leads to a better surface-to-volume ratio significant for the electrochemical processing while using it as electrode materials. A FESEM image of activated carbon (AC) in Fig. 5 shows the rough surface of carbon.

4.4. Electrochemical analysis

The electrochemical performance of M – 1 and M – 2 electrodes was evaluated through CV, GCD, and EIS using both three-electrode and two-electrode configurations [53,54]. In the three-electrode mode, a 1 M KOH aqueous electrolyte was employed, whereas Ag/AgCl served as the reference electrode and a platinum wire as the counter electrode.

4.4.1. Cyclic voltammetry

The CV measurements for both M – 1 and M – 2 at a scan rate limit of 5–50 mV/s with the potential window 0–0.5 V are shown in Fig. 6a and b. The presence of sharp oxidation and reduction peaks in the CV curves of both samples suggests Faradaic behavior [55]. Furthermore, the increased peak area and current with the increase in sweep rates exhibit pseudocapacitive behavior [56]. By evaluating the anodic peak

current as a function of $v^{1/2}$, the calculated regression coefficient (R^2) verifies the reversibility of the redox reactions at the electrode surface. Both M – 1 and M – 2 displayed a regression coefficient of 0.99 (approximately equal to 1), indicating high reversibility [57] of prepared samples as shown in Fig. 6c and d. Moreover, the b-value is determined by employing the power law as

$$i = av^b \quad \text{Eq 2}$$

Where ‘a’ and ‘b’ are variables, i is the peak current, and ‘v’ denotes the scan rate. The b-value is very useful in determining the electrode materials’ capacitive and battery-like nature. Through the graph between the log of peak current and the log of scan rate, the b-value, as the slope of the plot, is evaluated. The b-value between 0 and 0.5 indicates the battery-like nature of the material. If the b-value ranges between 0.8 and 1.0, the electrode material is good for capacitive applications. While for b-value between 0.5 and 0.8, a pseudocapacitive attribute to a mixture of capacitive and diffusive characteristics [58]. Electrode based on M – 1 has a b-value of 0.85, which shows that CeO_2 is capacitive and stores charge mainly through the EDLC mechanism, whereas M – 2 has a b-value of 0.56, which corresponds that the material is predominantly battery-like (Fig. 6e and f). It may be attributed to the fact that M – 2 stores charge mainly through Faradaic redox reactions due to the interconversion of dopant ions in it.

The comparative CV curves in Fig. 7a show high current and area under the curve, confirming the good electrochemical properties of M-2. The Dunns method indicates M – 2 is predominantly diffusion-controlled at low scan rates but with the increase scan rate the capacitive contribution is enhanced. When evaluating a material for high-power application, it is important to investigate how the material behaves at high scan rate and whether its composition facilitates kinetics. Therefore, Dunn’s method is further employed on M – 2 to determine quantitatively the capacitive and diffusive contribution of the electrode material. Capacitive contribution indicates the presence of EDLC behavior, while diffusive contribution indicates redox behavior [53]. Dunn’s method exhibited that the diffusion-controlled mechanism stands out to be a significant energy storage mechanism in M-2. Fig. 7b shows cyclic voltammograms for M – 2, affirming its capacitive, diffusive, and overall contribution. Fig. 7c shows that the sample has only 17 % capacitive contribution and 83 % diffusive contribution at 5 mV/s. The capacitive contribution continuously increased with an increase in scan rate and reached up to 40 % at a 100 mV/s scan rate. The values of capacitive and diffusive contributions determined through Dunn’s method by following the b-value confirm the pseudocapacitive nature of M-2. Specific capacitance of 111.9 F/g and 220.3 F/g for M – 1 and M – 2 were also calculated from CV curves which, showed a decrease with increasing scan rate.

4.4.2. Galvanostatic charge discharge (GCD)

GCD was employed at current densities with a limit of 0.5–2.5 A/g, discretely determined the charge capacity of M – 1 and M-2. The discharging curves for M – 1 and M – 2, displayed in Fig. 8a and b, show non-linear behavior with intermediate plateaus, indicating the presence of Faradaic redox reactions at the electrode surface. In correspondence with the CV, plateaus were more pronounced in the case of M – 2 compared to M – 1, indicating that M – 1 exhibits capacitive dominant energy storage, whereas M – 2 stores charge primarily through a diffusive mechanism. The preservation of the shape of GCD profiles confirmed the stability of the samples as well as significant reversibility. By Eq. (3) [59], specific capacitances were calculated.

$$C_s = \frac{2i \int V dt}{m \times V^2} \quad \text{Eq 3}$$

Here, $\int V dt$ denotes the area under the discharge curve, i/m denotes current density, and V is the switching potential. Fig. 8c shows that M – 2 has a significantly larger area under the curve and, therefore,

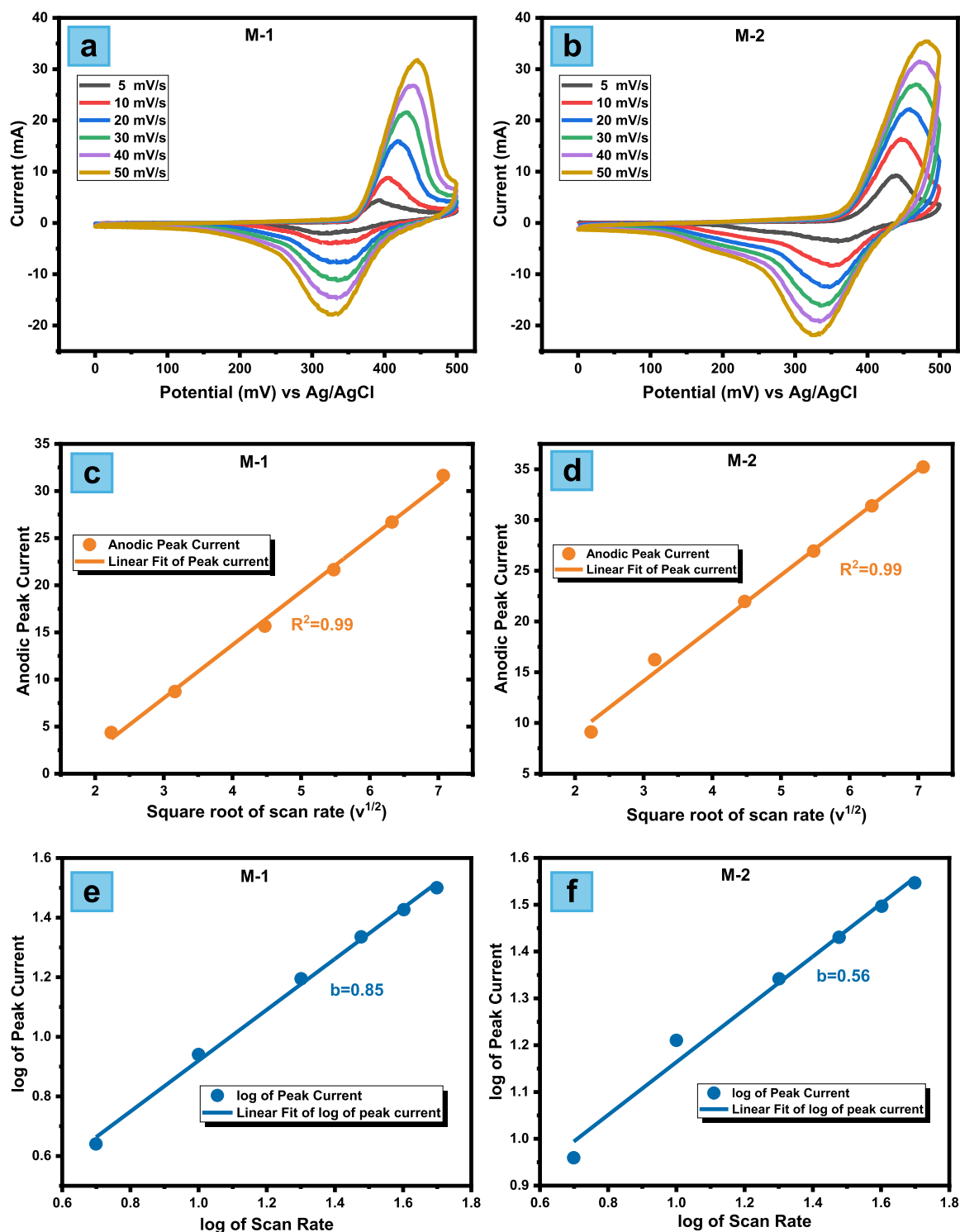


Fig. 6. (a) CV curves for M – 1 and (b) M – 2, (c) Linear regression coefficient for M – 1 and, (d) M – 2, (e) b-value for M – 1 and (f) M-2.

higher capacitance compared to M-1. M – 2 shows a maximum C_s of 244.4 F/g at 0.5 A/g as compared to 197.6 F/g of M-1. Fig. 8d shows the change in specific capacitances with the increase in current density.

4.4.3. Electrochemical impedance spectroscopy (EIS)

To understand the kinetics of electrochemical reactions depending on their internal resistance and charge storage mechanisms, EIS was

employed in a 0.1–100 kHz frequency range. Fig. 8e and f shows Nyquist plots and their fitted equivalent circuits for M – 1 and M – 2, respectively. The EIS spectrum for both M – 1 and M – 2 displayed a very small semicircle in a high-frequency region which is indicative of charge transfer resistance (R_{ct}), confirming the transfer of charge at electrode electrolyte interface (Faradaic redox reactions), while a linear curve in low-frequency region is indicative of the Warburg impedance (W_d)

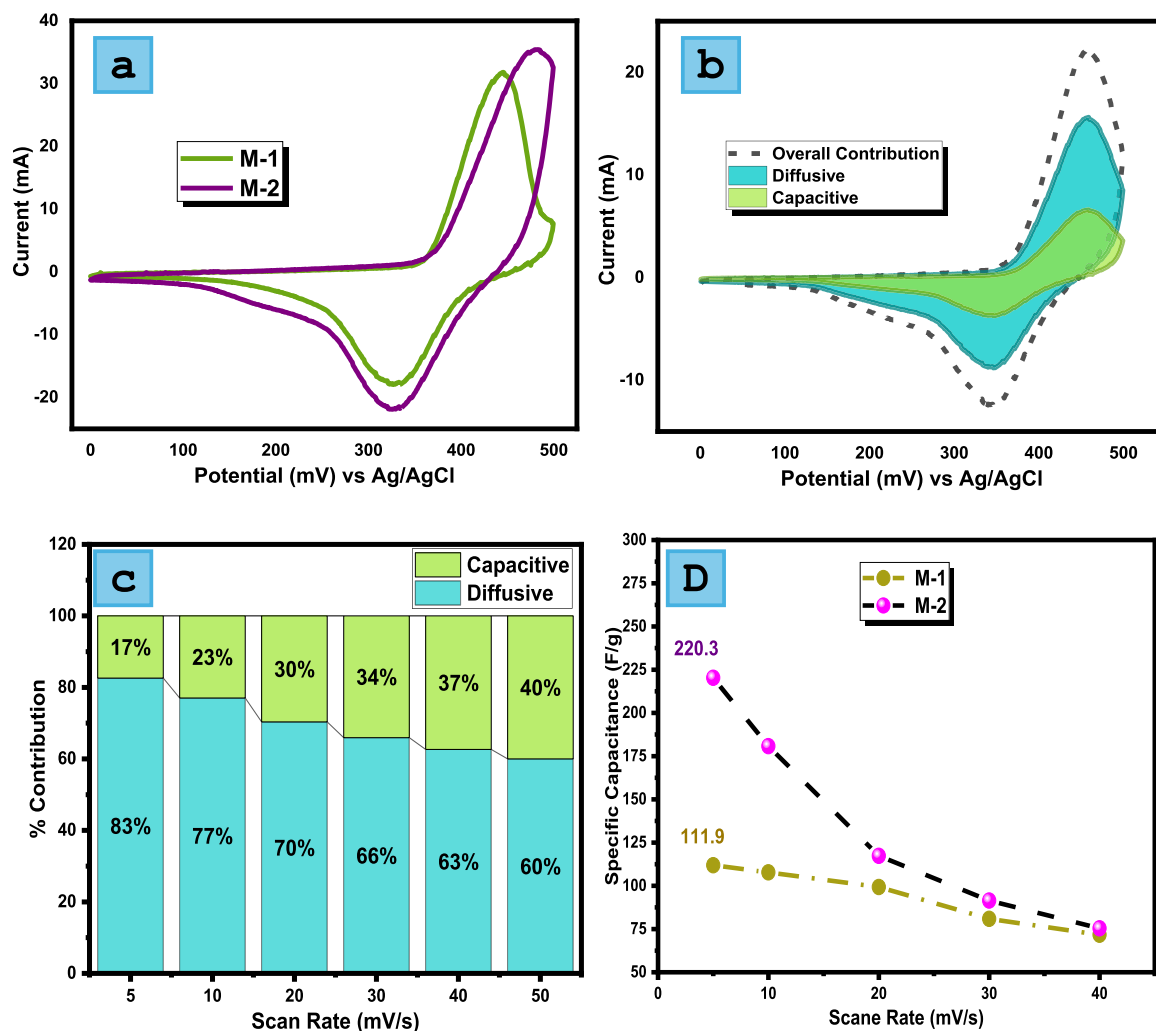


Fig. 7. (a) Comparative CV curves for M – 1 and M – 2, (b) Diffusive and capacitive contributions for M – 2 at 20 mV/s scan rate, and (c) percentage for both diffusive and capacitive contributions for M – 2 at various scan rates. (d) Specific capacitance calculated from CV curves of M – 1 and M-2.

demonstrating continuous diffusion of ions through pores of electrode and pseudocapacitive behavior of electrode material. Moreover, both samples show a small equivalent resistance (E_{sr}). M – 1 shows a small E_{sr} of 0.74Ω with R_{ct} of 61.7Ω , while M – 2 has E_{sr} of 1.2Ω with R_{ct} of 48.2Ω . The decrease in the R_{ct} of M – 2 as compared to M – 1 advocated the positive effect of Mg and Ni ions doping on CeO_2 .

4.5. Asymmetric hybrid device assembly

Electrochemical as well as structural characterization confirmed that the doping of divalent ions (Ni^{2+} and Mg^{2+}) in CeO_2 results in improved electrochemical properties of M-2. Hence, the best-performing sample M – 2 was then utilized for the fabrication of an asymmetric hybrid device. A hybrid device was fabricated by combining the M – 2 cathode as a positive electrode against the activated carbon (AC) anode as a negative electrode (Ni, Mg@ CeO_2 /AC).

4.5.1. Electrochemical analysis of hybrid device

CV analysis was conducted over a range of discrete scan rates (10 mV/s to 60 mV/s). The combined operational window for both M – 2 and activated carbon was selected and utilized (0 mV–1450 mV). Fig. 9a shows that cyclic voltammograms for the hybrid device are quasi-rectangular in shape with significant anodic and cathodic peaks.

The change in the shape of CV curves indicates the integration of the battery-like behavior of M – 2 and the EDLC behavior of activated carbon. Furthermore, the maintenance of the shapes of voltammograms validates good stability and exceptional rate capability.

The b-value of 0.72 is determined by the slope of the plot of the log of peak current versus the log of scan rates, which confirms the integration of EDLC behavior (Fig. 9b) [60]. Capacitive and diffusive contributions can also be estimated by Dunn's method. Results of Dunn's method, as shown in Fig. 9c, are in correspondence with the calculated b-value and CV curves. The increase in the value of capacitive contributions of the hybrid device as compared to the simple M – 2 sample is attributed to the capacitive behavior of the negative activated carbon electrode. The device showed a 28 % capacitive contribution and 72 % diffusive contribution at a 10 mV/s scan rate, as shown in Fig. 9d.

The working of the hybrid device, as shown in Fig. 10, is explained as follows. Since the M – 2 material-based hybrid supercapacitor has one electrode of the prepared co-doped ceria and the other one is taken as activated carbon. In the hybrid mode, the supercapacitor device exhibits a synergistic process of charge storage. The AC electrode plays its role in terms of charge transport, while the Ni, Mg co-doped CeO_2 /AC whereas the metal oxide contributes to charge storage via redox reactions. This combination results in superior specific capacitance and higher energy density compared to conventional supercapacitors. The pore structures

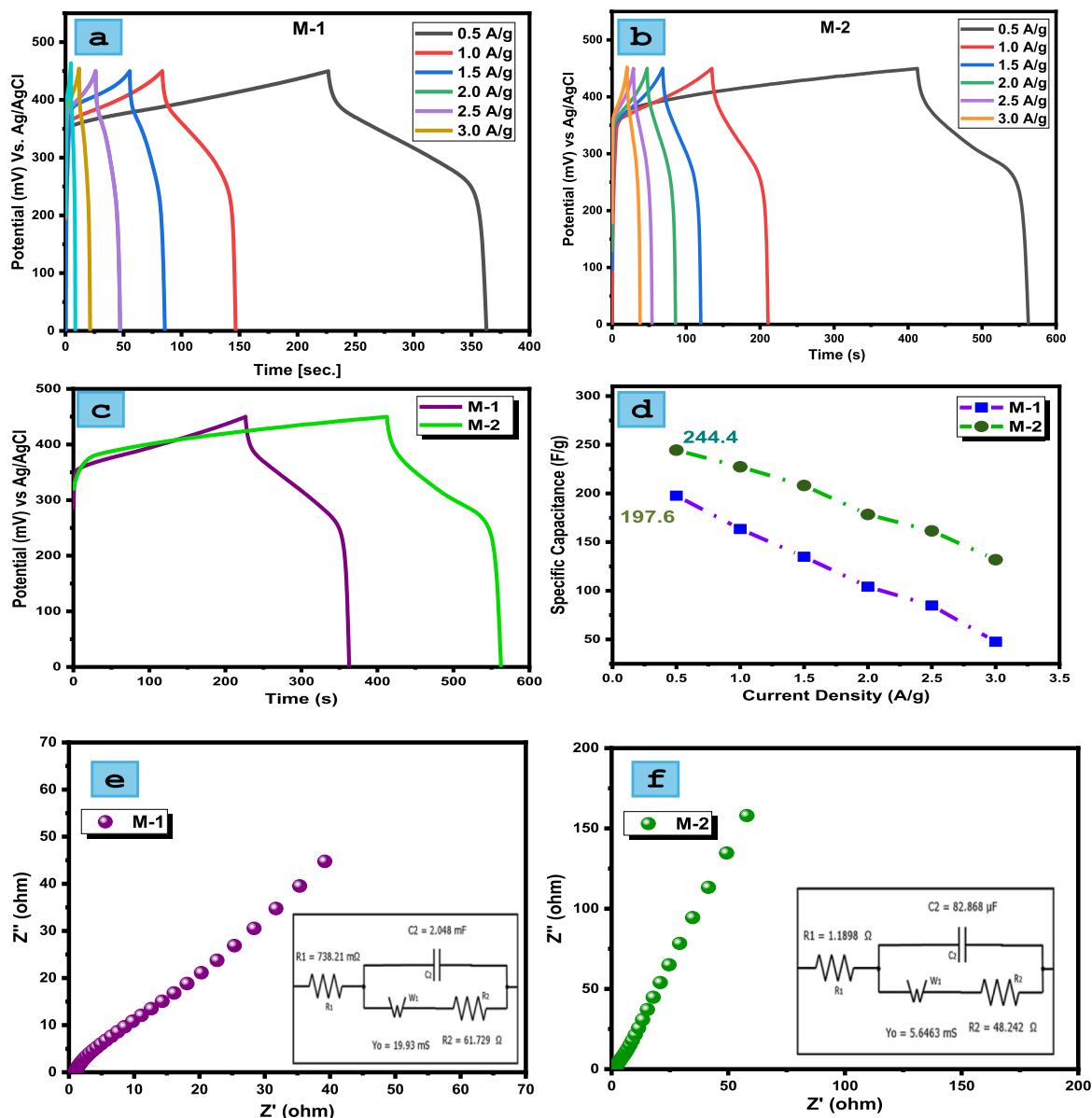


Fig. 8. (a) GCD profiles for M – 1, (b) GCD profiles for M – 2, (c) Comparison between GCD curves of M – 1 and M – 2, (d) C_s vs. current density, (e) Nyquist Plot with fitted equivalent circuit for M – 1 and (f) Nyquist Plot with fitted equivalent circuit for M-2.

of the metal oxide-based electrode and the AC electrode are critical for the ion adsorption. The charge accumulation is also between the capacitor electrode and electrolyte interface, leading to an effect on the overall conductivity. Further, the bonds of AC with the co-doped ceria may also sufficed passages for the fast electron dynamics [61]. Thus, the charge storage performance is improved.

GCD analysis was employed at various current densities (0.5 A/g to 3 A/g), and specific capacitance, energy density, and power density were estimated for the hybrid device. The plateaus in the middle of profiles, as shown in Fig. 11a, confirmed the occurrence of Faradaic redox reactions. The device exhibited a specific capacitance of 63.3 F/g at 0.5 A/g, which continuously decreases with the increase in current density, as shown in Fig. 11b. This is attributed to the fact that at higher current density, diffusion of electrolyte ions is restricted to the surface only, which ultimately results in a lower utilization of electrode material [62]. Specific energy and specific power were also calculated using Eqs. (4) and (5), respectively.

$$E = \frac{i \int V dt}{m \times 3.6} \quad \text{Eq 4}$$

$$P = \frac{E \times 3600}{t_d} \quad \text{Eq 5}$$

Here, i/m , $\int V dt$, and t_d denote the current density, the area under the discharge curve, and the discharge time, respectively. The fabricated hybrid device exhibits a maximum specific energy of 18.2 Wh/kg. Whereas 467.5 W/kg is the specific power at 0.5 A/g. Plotting specific energy and specific power against the current densities is shown in Fig. 11c, which depicts that the specific energy has a direct relation with current density, while specific power changes inversely with an increase in current density.

The stability and practical benefit of the fabricated device is assessed by applying 5000 continuous GCD cycles, as shown in Fig. 11d, which shows that the sample has a coulombic efficiency of 100.4 % over consecutive 5000 GCD cycles, placing it as an exceptional electrode

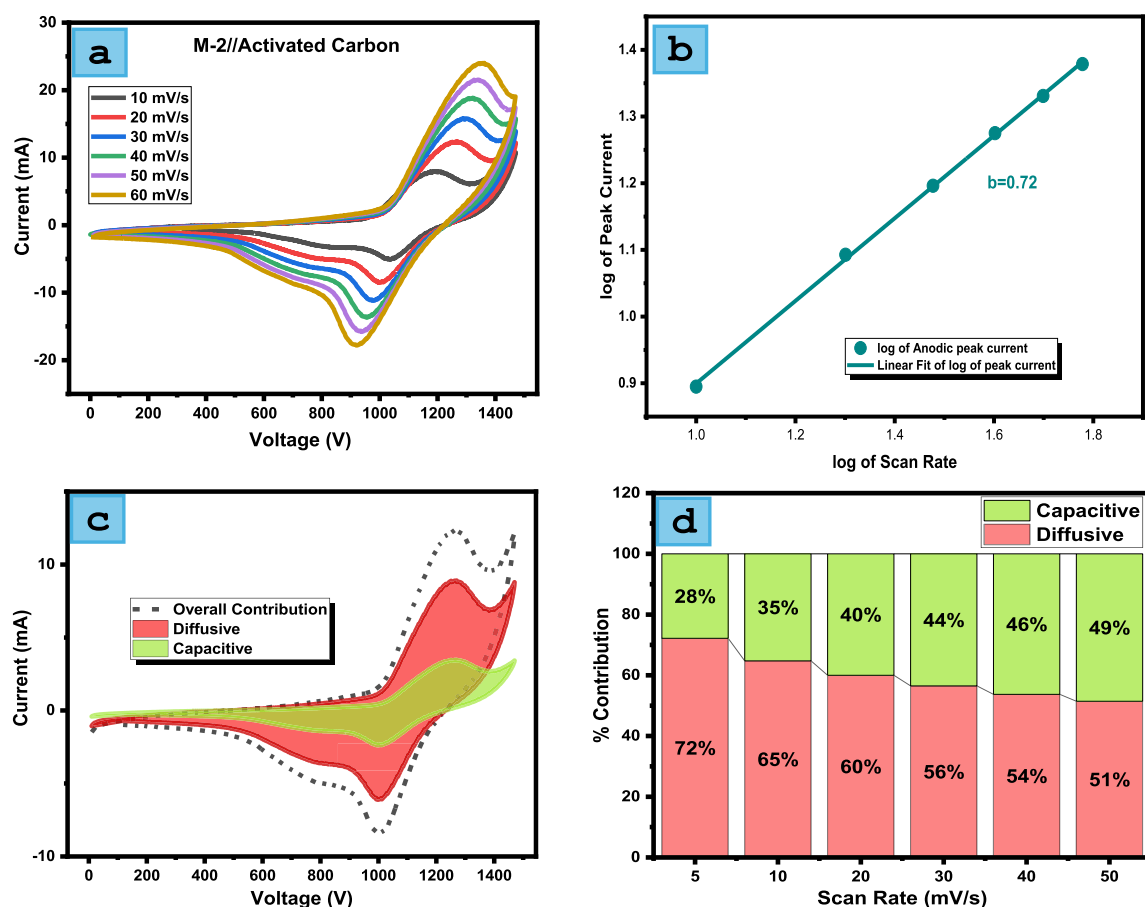


Fig. 9. (a) CV for M-2//Activated Carbon, (b) b-value for M-2//Activated Carbon, (c) Capacitive and diffusive contributions for M-2//Activated carbon at 20 mV/s scan rate, and (d) percentage contributions for M-2//Activated carbon at various scan rates.

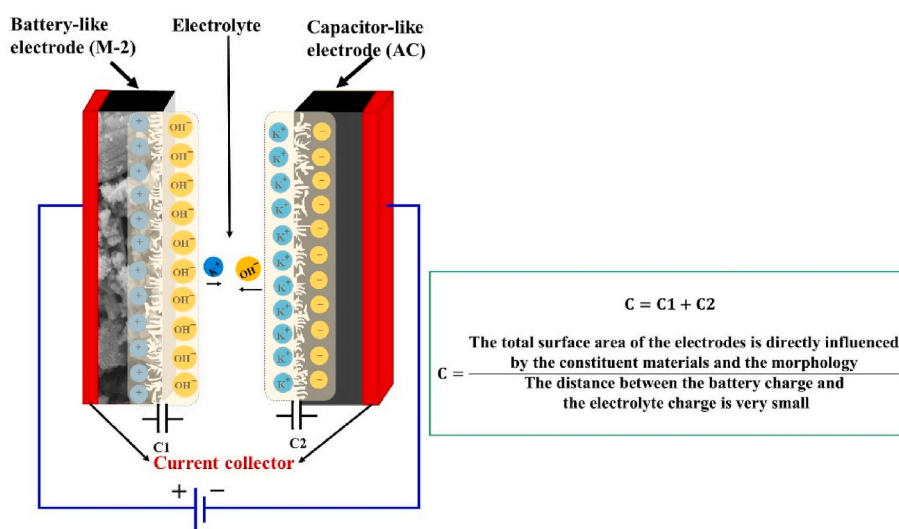


Fig. 10. Working of the hybrid supercapacitor device based on Ni, Mg co-doped ceria. The battery-like electrode and capacitor-like electrode both contribute to the final capacitance of the device.

material for energy storage. Since the hybrid device is run for 5000 GCD cycles at a current density of 10 A/g. At higher current density, the coulombic efficiency is usually recorded over 100 might be due to the system delay, redox shuttle and activation of Ni/Mg co-doped CeO_2 creates an abundance of vacancies to enhance ionic conductivity. During

GCD cycling, a beneficial surface reconstruction enables the electrolyte intercalation into the vacancy-rich regions, exposing more accessible redox active sites from both Ni and Ce, which increase charge storage capacity over time. Moreover, the ELC-based AC electrode serves as an efficient reversible counter electrode and provides rapid kinetics, which

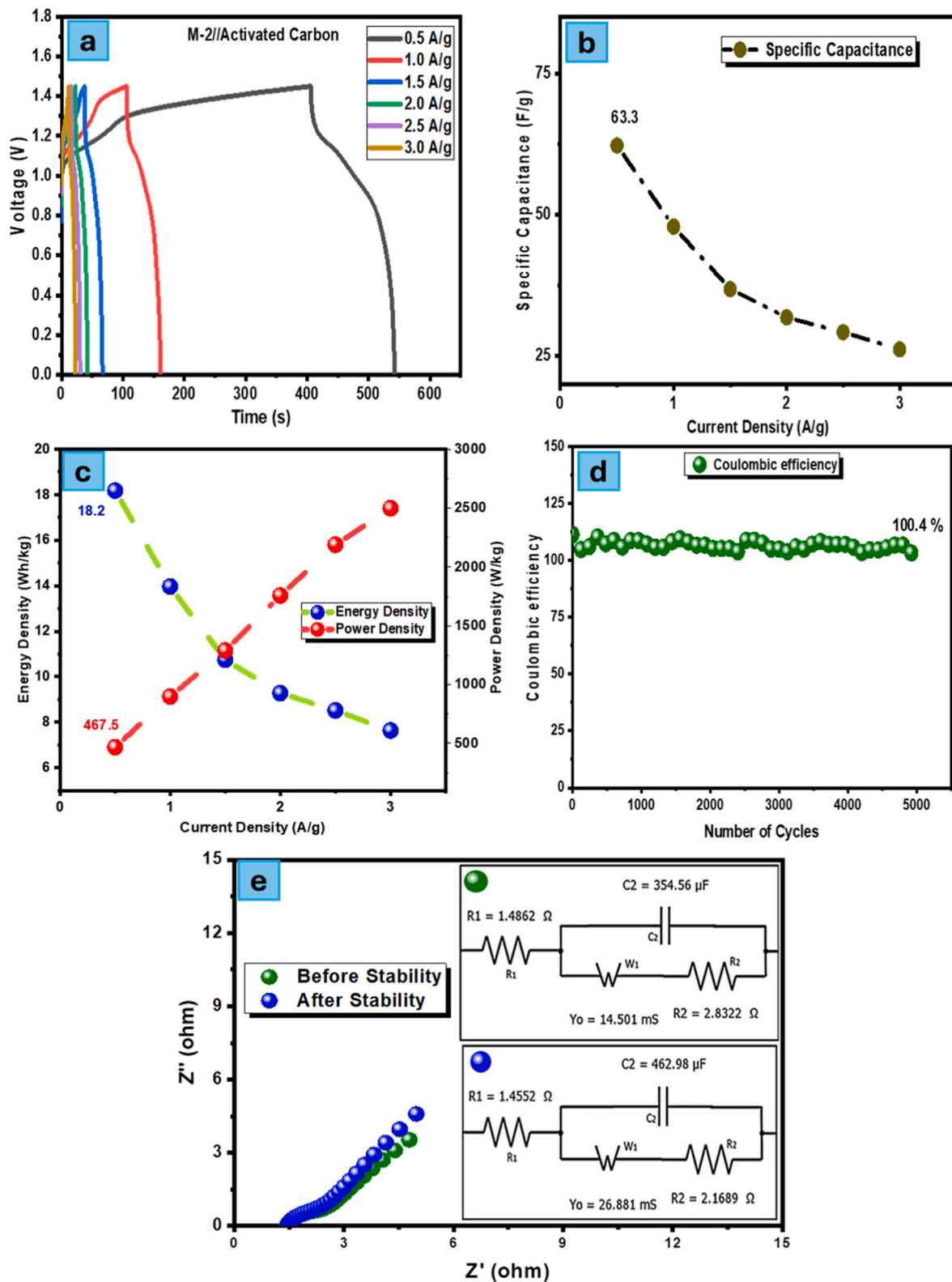


Fig. 11. (a) GCD curves for M-2//Activated Carbon, (b) specific capacitance of M-2//Activated Carbon device, (c) Specific Energy and Specific Power for M-2//Activated Carbon device, (d) Cyclic stability for M-2//Activated Carbon and (e) Nyquist plots and fitted equivalent circuits for M-2//Activated Carbon device before and after stability.

creates a low-stress environment for the M – 2 electrode. It also compensates for a slower diffusion-controlled Faradaic process. The synergistic effect enables the M – 2 electrode to safely activate and improve its performance, slightly exceeding the intrinsic material degradation

over time. As far as the device shows a constant value of coulombic efficiency, the device stability can be adjudged. The EIS analysis validates the superior performance and good electrical conductivity of the fabricated hybrid device. Nyquist plots before and after stability of the device

Table 1
Comparison with literature.

Ref.	Material	Synthesis	Specific capacitance (F/g)	Power density (W/kg)	Energy density (Wh/kg)	Retention
Current	Ni,Mg@CeO ₂ //AC	Solution combustion	244.4 (0.5 A/g)	467.5	18.3	100.4 % at 5000 GCD cycles
[18]	Cr-doped CeO ₂ nanoparticles	Chemical synthesis	42.6 (5 mV/s)	Not reported	Not reported	Not available
[63]	CeO ₂ /O-MoS ₂ composite	Wet synthetic	167.4 (0.5 A/g)	Not reported	Not reported	95.4 % after 4000 cycles
[64]	CeO ₂ -doped Zr nanoparticles	Ultrasonic method	198 (1 A/g)	Not reported	Not reported	>90 %
[37]	CeO ₂ /CNTs	Ultrasonic and hydrothermal	818 (1 mV/s)			95.3 % after 2000 cycles.
[40]	ZnO/CeO ₂ nanocomposite	Chemical precipitation	1069 (5 mV/s)	Not reported	39.6	Not reported
[35]	Ce _{1-x} Ni _x O ₂ (x = 0.1) nanoparticles	Combustion method	446	Not reported	Not reported	96.1 % after 2000 cycles
[31]	Mg-doped CeO ₂	Hydrothermal	131 C/g (1 A/g)	775	28.8	83 % after 9000 cycle
[29]	Ni-CeO ₂	Microwave-assisted	235 (2 A/g)	Not reported	Not reported	94 % after 1000 cycles

with their fitted equivalent circuits are shown on Fig. 11e. Both E_{sr} and R_{ct} decrease after stability, which confirms its good cyclic stability. There was no significant difference between the E_{sr} of the hybrid device (1.48 Ω and 1.45 Ω). However, the R_{ct} of 2.83 decreased to 2.17 Ω after the stability of the device. Current outcomes are compared with the literature in Table 1 as

Metal-organic frameworks (MOFs) have been widely explored and applied in many fields. However, the poor electrical conductivity of many traditional MOFs greatly limits their application in electrochemistry, especially in energy storage [65,66]. In this study, a typical cMOF (Ni-HHTP, HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) was compounded with MXene nanosheets and a series of composites, namely MXene@Ni-HHTP- x ($x = 1-8$), were obtained. As a result, when MXene@Ni-HHTP-2 was assembled as a positive electrode material in an asymmetric supercapacitor, it achieved a specific capacitance of 416.6 F/g at 0.5 A g⁻¹, manifesting a good performance in energy storage.

5. Conclusion

In this study, CeO₂ has been successfully utilized as a base material for developing high-performance electrodes through a facile solution combustion synthesis. To investigate the influence of dopants, Ni and Mg were co-doped into the CeO₂ matrix, and their electrochemical effects were systematically studied. The synthesized materials exhibited spherical morphology with a well-defined face-centered cubic (FCC) crystal structure. Notably, the co-doped Ni, Mg @ CeO₂ (M-2) demonstrated superior charge storage capability, delivering a **specific capacitance of 244.4 F/g at 0.5 A/g**, compared to 197.6 F/g for undoped CeO₂ (M-1). Furthermore, the assembled supercapacitor device, configured by **Ni, Mg@ CeO₂/AC (M-2)**, achieved an impressive **specific energy of 18.3 Wh/kg and specific power of 467.5 W/kg at 0.5 A/g** while maintaining exceptional cycling stability, evidenced by a **Coulombic efficiency of 100.4 % over 5000 GCD cycles**.

CRediT authorship contribution statement

Muddasira Sarwar: Investigation, Methodology, Writing – original draft. **Muhammad Shahbaz:** Validation, Visualization, Writing – original draft. **Rabia Ghaffar:** Writing – original draft. **Mohsin Saleem:** Methodology, Validation, Visualization, Writing – original draft. **Muhammad Zubair Khan:** Writing – original draft. **Muneeb Irshad:** Writing – original draft. **Shahzad Sharif:** Writing – original draft. **Jung Hyuk Koh:** Writing – original draft. **Muhammad Haseeb:** Writing – original draft. **Abdul Ghaffar:** Investigation, Methodology, Supervision, Writing – original draft. **Imran Shakir:** Writing – original draft. **Kamran Ali:** Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was jointly supported by the National Research Program of Universities (NRPU), the Higher Education Commission, (HEC), Pakistan research fund “Development of lab/pilot scale facilities for the production of piezoelectric material for multilayer energy devices” 20-15673/NRPU/R&D/HEC/2021 and MSIT (Ministry of Science and ICT), Korea, under the ITRC (Information Technology Research Centre) support program (IITP-2025-RS-2020-II201655, 50 %) supervised by the IITP (Institute of Information and Communications Technology Planning And Evaluation).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtsust.2025.101272>.

Data availability

Data will be made available on request.

References

- [1] J.E. Duggan, Recent progress in sustainable energy systems development: investment, operations, and decarbonization, *Curr Sustainable Renewable Energy Rep* 12/1 (2025), <https://doi.org/10.1007/s40518-024-00248-3>.
- [2] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.* 19/11 (2020) 1151–1163, <https://doi.org/10.1038/s41563-020-0747-z>.
- [3] S. Kirsch, Running out? Rethinking resource depletion, *Extr. Ind. Soc.* 7/3 (2020) 838–840, <https://doi.org/10.1016/j.exis.2020.06.002>.
- [4] M.K. Khan, M. Raza, M. Shahbaz, U. Farooq, M.U. Akram, Recent advancement in energy storage technologies and their applications, *J. Energy Storage* 92 (2024) 112112, <https://doi.org/10.1016/j.est.2024.112112>.
- [5] M. Feng, Y. Liu, X. Wu, Y. Xing, Q. Chi, Film capacitor materials for electric vehicle applications: status quo and future prospects, *Prog. Mater. Sci.* 152 (2025) 101458, <https://doi.org/10.1016/j.pmatsci.2025.101458>.
- [6] L. Liu, X. Zhang, Y. Liu, X. Gong, Electrochemical energy storage devices—Batteries, supercapacitors, and battery-supercapacitor hybrid devices, *ACS Appl. Electron. Mater.* 7/6 (2025) 2233–2270, <https://doi.org/10.1021/acsaem.5c00069>.
- [7] A.A. Khan, M.S. Habib, M.A. Rafiq, A. Maqbool, M.A. Hussain, R.A. Malik, M. Saleem, I.H. Khan, M. Nawaz, Exploring thermally stable dielectric and energy storage response of Bi-based ceramics for renewable energy storage applications, *J. Electroceram.* (2025), <https://doi.org/10.1007/s10832-025-00402-3>.
- [8] N. Parvin, M. Dhananjaya, M. Kang, S. Joo, J.H. Jung, T.K. Mandal, Recent advances in hybrid supercapacitors: a review of high performance materials and scalable fabrication techniques, *J. Mater. Chem. A* (2025), <https://doi.org/10.1039/D5TA02887F>.
- [9] S. Sagadevan, A.R. Marlinda, Z.Z. Chowdhury, Y.B.A. Wahab, N.A. Hamizi, M. Shahid, F. Mohammad, J. Podder, M.R. Johan, Ch.2-Fundamental electrochemical energy storage systems, in: N. Arshid, M. Khalid, A.N. Grace (Eds.),

- Advances in Supercapacitor and Supercapattery, 2021, pp. 27–43, <https://doi.org/10.1016/B978-0-12-819897-1.00001-X>.
- [10] Y. Xu, Y. Jiang, X. Yu, Y. Gu, M. Shakouri, R. Zhu, H. Pang, Synergistic Ni-Co metal nodes in a conjugated MOF-modified separator for high-performance lithium-sulfur batteries, *Adv. Sci.* (2025) e13282, <https://doi.org/10.1002/advsc.20251282>.
 - [11] C. Wang, J. Hao, L. Duan, D. Zhao, Y. Ma, J. Zhang, F. Meng, Energy storage performance with ultrahigh energy density and power density of $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_{3-x}$ -based lead-free ceramics through synergistic optimization, *Ceram. Int.* 51 (21, Part B) (2025) 35133–35143, <https://doi.org/10.1016/j.ceramint.2025.05.237>.
 - [12] H.R. Khan, A.L. Ahmad, Supercapacitors: overcoming current limitations and charting the course for next-generation energy storage, *J. Ind. Eng. Chem.* 141 (2025) 46–66, <https://doi.org/10.1016/j.jiec.2024.07.014>.
 - [13] O. Gohar, H.A. Ishaq, M.A. Iqbal, M.Z. Khan, S. Basharat, N. Kanwal, A. Riaz, M. Saleem, J.-H. Koh, I. Hussain, M.A. Akram, Recent advancements in high-performance and durable electrodes materials for magnesium-ion batteries, *Coord. Chem. Rev.* 538 (2025) 216702, <https://doi.org/10.1016/j.ccr.2025.216702>.
 - [14] M. Shahbaz, S. Sharif, T.T.R. Afzal, S. Shahzad, A. Shahzad, O. Şahin, A. Bentalib, A.B. Jumah, S. Hussain, N.A. Khan, Construction of rectangular microporous Cerium 3D metal organic framework for high performance energy storage devices, *J. Solid State Chem.* 348 (2025) 125394, <https://doi.org/10.1016/j.jssc.2025.125394>.
 - [15] S. Jayakumar, P.C. Santhosh, M.M. Mohideen, A.V. Radhamani, A comprehensive review of metal oxides (RuO_2 , Co_3O_4 , MnO_2 and NiO) for supercapacitor applications and global market trends, *J. Alloys Compd.* 976 (2024) 173170, <https://doi.org/10.1016/j.jallcom.2023.173170>.
 - [16] Himadri Tanaya Das, T. Elango Balaji, Swapnamoy Dutta, Nigamananda Das, Payaswini Das, Aniruddha Mondal, Muhammad Imran, Recent trend of CeO_2 -based nanocomposites electrode in supercapacitor: a review on energy storage applications, *J. Energy Storage* 50 (2022) 104643, <https://doi.org/10.1016/j.est.2022.104643>.
 - [17] S. Kumar, F. Ahmed, N. Ahmad, N.M. Shaalan, R. Kumar, A. Alshoaibi, N. Arshi, S. Dalela, P.A. Alvi, K. Kumari, Influence of Fe and Cu Co-Doping on structural, magnetic and electrochemical properties of CeO_2 nanoparticles, *Materials* 15/12 (2022) 4119, <https://doi.org/10.3390/ma15124119>.
 - [18] B. Veena, S. Pavithra, M. Seetha, A. Sakunthala, Yoshitake Masuda, Cr doped CeO_2 nanoparticles as supercapacitor electrodes, *AIP Adv.* 12/12 (2022) 125310, <https://doi.org/10.1063/5.0130499>.
 - [19] N. Maheswari, G. Muralidharan, Supercapacitor behavior of cerium oxide nanoparticles in neutral aqueous electrolytes, *Energy Fuels* 29/12 (2015) 8246–8253, <https://doi.org/10.1021/acs.energyfuels.5b02144>.
 - [20] A.A.G. Santiago, N.F.A. Neto, E. Longo, C.A. Paskocimas, F.V. Motta, M.R. D. Bomio, Fast and continuous obtaining of Eu^{3+} doped CeO_2 microspheres by ultrasonic spray pyrolysis: characterization and photocatalytic activity, *J. Mater. Sci. Mater. Electron.* 30 (2019) 11508–11519, <https://doi.org/10.1007/s10854-019-01506-7>.
 - [21] I. Shown, A. Ganguly, L.-C. Chen, K.-H. Chen, Conducting polymer-based flexible supercapacitor, *Energy Sci. Eng.* 3 (1) (2015) 2–26, <https://doi.org/10.1002/ese3.50>.
 - [22] C. Chang Hu, K. Hsin Chang, M. Champ Lin, Y. Tai Wu, Design and tailoring of the nanotubular arrayed architecture of hydrous RuO_2 for next generation supercapacitors, *Nano Lett.* 6/12 (2006) 2690–2695, <https://doi.org/10.1021/nl061576a>.
 - [23] X.Y. Feng, C. Shen, Y. Yu, S.Q. Wei, C.H. Chen, Synthesis and electrochemical properties of sticktight-like and nanosheet Co_3O_4 particles, *J. Power Sources* 230 (2013) 59–65, <https://doi.org/10.1016/j.jpowsour.2012.12.046>.
 - [24] K. Wu, J. Zhao, X. Zhang, H. Zhou, M. Wu, Hierarchical mesoporous MoO_3 sphere as highly effective supercapacitor electrode, *J. Taiwan Inst. Chem. Eng.* 102 (2019) 212–217, <https://doi.org/10.1016/j.jtice.2019.06.002>.
 - [25] S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, Graphene Oxide– MnO_2 nanocomposites for supercapacitors, *ACS Nano* 4/5 (2010) 2822–2830, <https://doi.org/10.1021/nn901311t>.
 - [26] K.C. Ugochi, C.N. Agnes, S. Ezugwu, A.C. Nwanya, N.M. Shinde, M. Kebede, P. M. Ejikeme, M. Maaza, F.I. Ezema, Recent progress in nickel oxide-based electrodes for high-performance supercapacitors, *Curr. Opin. Electrochem.* 21 (2020) 175–181, <https://doi.org/10.1016/j.coelec.2020.02.004>.
 - [27] K. Prasanna, P. Santhoshkumar, Y.N. Jo, I.N. Sivagami, S.H. Kang, Y.C. Joe, C. W. Lee, Highly porous CeO_2 nanostructures prepared via combustion synthesis for supercapacitor applications, *Appl. Surf. Sci.* 449 (2018) 454–460, <https://doi.org/10.1016/j.apsusc.2017.12.130>.
 - [28] N. Padmanathan, S. Selladurai, Shape controlled synthesis of CeO_2 nanostructures for high performance supercapacitor electrodes, *RSC Adv.* 4 (2014) 6527–6534, <https://doi.org/10.1039/C3RA43339K>.
 - [29] R. Murugan, G. Ravi, G. Vijayaprasath, S. Rajendran, M. Thaiyan, M. Nallappan, M. Gopalanb, Y. Hayakawa, Ni– CeO_2 spherical nanostructures for magnetic and electrochemical supercapacitor applications, *Phys. Chem. Chem. Phys.* 19 (2017) 4396–4404, <https://doi.org/10.1039/C6CP08281E>.
 - [30] Q. Gong, Y. Li, H. Huang, J. Zhang, T. Gao, G. Zhou, Shape-controlled synthesis of Ni– CeO_2 @PANI nanocomposites and their synergetic effects on supercapacitors, *Chem. Eng. J.* 344 (2018) 290–298, <https://doi.org/10.1016/j.cej.2018.03.079>.
 - [31] K. Hussain, I. Ali, S. Hasnain, S.S. Hussain, B. Hussain, M.S. Khan, S.M. Ammar, B. Hussain, A. Hussain, M.A. Javed, A. Ullah, S.A. Arni, N. Elboughdiri, N. Abbas, Reagents assisted Mg-doped CeO_2 for high-performance energy-storage applications, *J. Electroanal. Chem.* 873 (2020) 114401, <https://doi.org/10.1016/j.jelechem.2020.114401>.
 - [32] M. Vanitha, Keerthi, P. Cao, N. Balasubramanian, Ag nanocrystals anchored CeO_2 /graphene nanocomposite for enhanced supercapacitor applications, *J. Alloys Compd.* 644 (2015) 534–544, <https://doi.org/10.1016/j.jallcom.2015.03.221>.
 - [33] H. Duan, T. Wang, X. Wu, Z. Su, J. Zhuang, S. Liu, R. Zhu, C. Chen, H. Pang, CeO_2 quantum dots doped Ni-Co hydroxide nanosheets for ultrahigh energy density asymmetric supercapacitors, *Chin. Chem. Lett.* 31/9 (2020) 2330–2332, <https://doi.org/10.1016/j.ccl.2020.06.001>.
 - [34] N. Zahra, M. Shahbaz, M. Saleem, M.Z. Khan, M. Irshad, S. Sharif, J.H. Koh, M. A. Marwat, G. Lee, M. Irfan, A. Ghaffar, Innovative multiphase composites of transition metal oxides for long-term stability and high energy density in storage devices, *Mater. Today Sustain.* 30 (2025) 101099, <https://doi.org/10.1016/j.mtsust.2025.101099>.
 - [35] J. Alex, S. Rajkumar, J.P. Merlin, A. Aravind, D. Sajan, C.S. Praveen, Single step auto-igniting combustion technique grown CeO_2 and Ni-doped CeO_2 nanostructures for multifunctional applications, *J. Alloys Compd.* 882 (2021) 160409, <https://doi.org/10.1016/j.jallcom.2021.160409>.
 - [36] N. Ahmad, A.A. Alghamdi, H.A. Al-Abdulkarim, G.M. Mustafa, N. Baghdadi, F. A. Alharthi, F.A. Structural, Morphological, and electrochemical performance of CeO_2 /NiO nanocomposite for supercapacitor applications, *Appl. Sci.* 11 (2021) 411, <https://doi.org/10.3390/app11010411>.
 - [37] Y. Luo, T. Yang, Q. Zhao, M. Zhang, CeO_2 /CNTs hybrid with high performance as electrode materials for supercapacitor, *J. Alloys Compd.* 729 (2017) 64–70, <https://doi.org/10.1016/j.jallcom.2017.09.165>.
 - [38] L.S. Aravinda, K.U. Bhat, B.R. Bhat, Nano CeO_2 /activated carbon based composite electrodes for high performance supercapacitor, *Mater. Lett.* 112 (2013) 158–161, <https://doi.org/10.1016/j.matlet.2013.09.009>.
 - [39] W. Wu, W. Qi, Y. Zhao, X. Tang, Y. Qiu, D. Su, H. Fan, G. Wang, Hollow CeO_2 spheres conformally coated with graphitic carbon for high-performance supercapacitor electrodes, *Appl. Surf. Sci.* 463 (2019) 244–252, <https://doi.org/10.1016/j.apsusc.2018.08.224>.
 - [40] S.S. Arunpandian, S. Bharathi, A. Pandikumar, S.E. Arasi, A. Arivaranan, Structural analysis and redox additive electrolyte based supercapacitor performance of ZnO/CeO_2 nanocomposite, *Mater. Sci. Semicond. Process.* 106 (2020) 104765, <https://doi.org/10.1016/j.mssp.2019.104765>.
 - [41] K.O. Abdulwahab, M.M. Khan, J.R. Jennings, Doped ceria nanomaterials: preparation, properties, and uses, *ACS Omega* 8/34 (2023) 30802–30823, <https://doi.org/10.1021/acsomega.3c01199>.
 - [42] M. Chen, H. Gao, L. Zhang, Y. Xuan, J. Ren, M. Ni, Z. Lin, Unlocking the nature of the co-doping effect on the ionic conductivity of CeO_2 -based electrolyte, *Ceram. Int.* 45/3 (2019) 3977–3985, <https://doi.org/10.1016/j.ceramint.2018.11.072>.
 - [43] S.S. Kang, J. Yang, B.B. Yang, X.J. Zhan, Y.M. Zhang, Y.Q. Dai, D.P. Song, Enhanced electrostatic energy storage through a multi-element doping design, *Appl. Phys. Lett.* 122 (4) (2023) 042902, <https://doi.org/10.1063/5.0135242>.
 - [44] Y. Sun, K. Kurosaki, T. Imamura, R. Torata, Y. Ohishi, D. Palaporn, T. Nachaithong, S. Pinitsoontorn, J. Padchasi, P. Kidkhunthod, M. Suwannaruang, S. Tanusilp, Investigating thermoelectric properties of GeTe alloys with multi element doping: insights from high-entropy engineering, *ACS Omega* 10/29 (2025) 32112–32121, <https://doi.org/10.1021/acsomega.5c03826>.
 - [45] Z. Li, W. Xi, Z. Jiang, Y. Zhang, R. Wang, Y. Gong, H. Wang, J. Jin, Multi-element doping regulation of the disordered phase transition and multi-step phase transition suppression effect in O_3 -Type sodium-ion batteries, *Small* 21/40 (2025) e06854, <https://doi.org/10.1002/smll.202506854>.
 - [46] K. Akhmetova, F. Sultanov, A. Mentbayeva, N. Umirov, Z. Bakenov, B. Tatyayev, Advances in multi-element doping of LiFePO_4 cathode material for capacity enhancement in Li-ion batteries, *J. Power Sources* 624 (2024) 235531, <https://doi.org/10.1016/j.jpowsour.2024.235531>.
 - [47] R. Zhu, Y. Gu, L. Liu, J. Lu, H. Pang, Integration of conductive MOF and MXene for high-performance supercapacitor, *New J. Chem.* 48/23 (2024) 10593–10598, <https://doi.org/10.1039/D3NJ05392J>.
 - [48] L. Liu, Y. Zhang, Y. Song, Y. Gu, H. Pang, R. Zhu, Successful in situ growth of conductive MOFs on 2D cobalt-based compounds and their electrochemical performance, *Inorg. Chem.* 63/22 (2024) 10324–10334, <https://doi.org/10.1021/acs.inorgchem.4c01168>.
 - [49] M. Shahbaz, S. Sharif, M.W. Mushtaq, Z. Ghaznavi, Z. Iqbal, M.A. Khurshid, O. Şahin, S. Shahzad, M. Saeed, A. Shahzad, Improved electrochemical performance of nitrogen-containing copper-based 1D metal organic framework derived from highly connective pyridine-2,4,6-tricarboxylic acid for hybrid supercapacitors, *J. Mater. Chem. A* 13 (2025) 6524–6538, <https://doi.org/10.1039/d4ta05425c>.
 - [50] R. Ganjoo, S. Sharma, A. Kumar, M.M.A. Daouda, in: C. Verma, M.A. Quraishi (Eds.), *Activated Carbon Progress and Applications*, The Royal Society of Chemistry, 2023, pp. 1–22, <https://doi.org/10.1039/BK9781839169861-00001>, ch. 1.
 - [51] C.M. Magdalane, K. Kaviyarasu, G.M.A. Priyadharsini, A.K.H. Bashir, N. Mayedwa, N. Matinise, A.B. Isaev, N.A. Al-Dhahi, M.V. Arasu, S. Arokiasari, J. Kennedy, M. Maaza, Improved photocatalytic decomposition of aqueous Rhodamine-B by solar light illuminated hierarchical yttria nanosphere decorated ceria nanorods, *J. Mater. Res. Technol.* 8 (3) (2019) 2898–2909, <https://doi.org/10.1016/j.jmrt.2018.11.019>.
 - [52] G. Wang, Q. Mu, T. Chen, Y. Wang, Synthesis, characterization and photoluminescence of CeO_2 nanoparticles by a facile method at room temperature, *J. Alloys Compd.* 493 (1–2) (2010) 202–207, <https://doi.org/10.1016/j.jallcom.2009.12.053>.
 - [53] A.A. Starodubtseva, Y.S. Zhigalenok, K.M. Maldybaev, A.K. Galeyeva, I.A. Trussov, A.P. Kurbatov, On electrochemistry of metal–organic framework $\text{Zn}_2(\text{EDTA})(\text{H}_2\text{O})$, *RSC Adv.* 13 (2023) 4880–4889, <https://doi.org/10.1039/D3RA00040K>.

- [54] S. Li, X. Zhan, W. Bai, J. Zheng, Controllable synthesis of Ni/Co-TCP MOFs with different morphologies and their application in electrochemical detection of glucose, *J. Electrochem. Soc.* 167 (2020) 127506, <https://doi.org/10.1149/1945-7111/abac2a>.
- [55] Z. Zhang, Z. Wang, M. Dong, Q. Zhu, K.H. Klausen, Synergistic enhancement of supercapacitors with cobalt–copper bimetal–organic framework, *Adv. Eng. Mater.* 26 (2024) 2400378, <https://doi.org/10.1002/adem.202400378>.
- [56] S. Khan, S. Chand, P. Sivasakthi, P.K. Samanta, C. Chakraborty, A highly robust and conducting ultramicroporous 3D Fe(II)-Based metal–organic framework for efficient energy storage, *Small* 20 (2024) 2401102, <https://doi.org/10.1002/sml.202401102>.
- [57] M.W. Mushtaq, M. Shahbaz, R. Naeem, S. Bashir, S. Sharif, K. Alia, N.A. Dogar, Synthesis of surfactant-assisted nickel ferrite nanoparticles (NFNPs@surfactant) to amplify their application as an advanced electrode material for high-performance supercapacitors, *RSC Adv.* 14 (2024) 20230–20239, <https://doi.org/10.1039/D4RA02135E>.
- [58] K. Chen, D. Xue, Colloidal paradigm in supercapattery electrode systems, *Nanotechnology* 29 (2018) 024003, <https://doi.org/10.1088/1361-6528/aa9bfd>.
- [59] M. Anwar, A. Fazal, M.J. Iqbal, B.S. Almutairi, M.Z. Khan, M. Irshad, M.A. Raza, M. S. Butt, M. Saleem, W. Ahmed, A. Ghaffar, Solution-combustion synthesis of AgCo₃O₄/FeMn-O multiphase composite for high-performance asymmetric supercapacitor, *J. Energy Storage* 105 (2025) 114602, <https://doi.org/10.1016/j.est.2024.114602>.
- [60] M. Sathya A.S. Prakash, K. Ramesha, J. –M. Tarascon, A.K. Shukla, V₂O₅-Anchored carbon nanotubes for enhanced electrochemical energy storage, *J. Am. Chem. Soc.* 133/40 (2011) 16291–16299, <https://doi.org/10.1021/ja207285b>.
- [61] R.G. Bobade, N.B. Dabke, S.F. Shaikh, A.M. Al-Enizi, B. Pandit, B.J. Lokhande, R. C. Ambare, Concentration-dependent SILAR synthesized Di-bismuth copper oxide nanomaterials electrode in asymmetric supercapacitor, *J. Mater. Sci. Mater. Electron.* 35 (2024) 129, <https://doi.org/10.1007/s10854-023-11818-4>.
- [62] J. Wang, M. Rao, C. Ye, Y. Qiu, W. Su, S. Zheng, J. Fan, S. Cai, W.-G. Zhang, Cu-MOF derived Cu–C nanocomposites towards high performance electrochemical supercapacitors, *RSC Adv.* 10 (2020) 4621–4629, <https://doi.org/10.1039/C9RA09738D>.
- [63] S. Suresh, V. Sindhu, Enhanced gravimetric capacitance of CeO₂ by compositing with the hybridized phase of MoS₂, *Ionics* 29 (2023) 843–852, <https://doi.org/10.1007/s11581-022-04846-3>.
- [64] M.V. Arularasu, T.V. Rajendran, B. Arkook, M. Harb, K. Kaviyarasu, Enhanced electrochemical performance of highly porous CeO₂-Doped Zr nanoparticles for supercapacitor applications, *Microsc. Res. Tech.* 88/3 (2025) 621–630, <https://doi.org/10.1002/jemt.24728>.
- [65] M. Zhang, J. Fu, N. Xu, L. Meng, A dual-modification strategy for both the Quinone-based cathode and Zn anode electrodes of the aqueous zinc-ion battery, *Chem. Eng. J.* 511 (2025) 161944, <https://doi.org/10.1016/j.cej.2025.161944>.
- [66] J. Yan, M. Cen, Y. Guo, B. Wang, Y. Tian, Z. Song, D.H.L. Ng, Highly sulfur-doped porous carbon enhances sodium-ion storage with superior rate capability and long cycling stability, *J. Mater. Sci.* 60 (41) (2025) 19883–19895, <https://doi.org/10.1007/s10853-025-11633-8>.