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CeO₂ Nanoparticles: A New High Performance Electrode Material for Supercapacitors

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Abstract: CeO₂ nanoparticles have been synthesized via hydrothermal method using CTAB as the capping agent. The as prepared cerium oxide was annealed in air at different temperatures (300, 400 and 500°C). X-ray diffraction patterns indicate the formation of CeO₂ nanoparticles in the cubic fluorite structure. FTIR spectra further confirm the formation of Ce–O bonds. Electrochemical investigation of the electrodes fabricated using CeO₂ was carried out using cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. From cyclic voltammetry analysis CeO₂–400 was found to exhibit the specific capacitance of 526 F g⁻¹ at a scan rate of 5 mV s⁻¹. The charge transfer resistance of CeO₂–400 was found to be 0.29Ω. These results indicate that CeO₂ annealed at 400°C is a promising electrode material for supercapacitor applications.

Keywords: CeO₂ Nanoparticles, High Performance Electrode Material, Supercapacitors.

Introduction

The ever-increasing need for energy and its consumption has motivated a serious search for alternative sources of energy that are clean and sustainable. Supercapacitors have attracted the attention of a large number of researchers owing to their larger energy density compared to traditional dielectric capacitors and their greater power density than rechargeable batteries, as well as their exceedingly good cycle life¹. The fabrication of smart electrochemical capacitors or supercapacitors with superior electrode materials is one of the prime tasks taken up by material scientists. Nanostructured electrode materials have large surface area and good porosity that help to improve the electrochemical performance of a supercapacitor². Various materials such as transition metal oxides, conducting polymers and high surface area carbonaceous materials have been investigated for supercapacitor applications³. Ruthenium oxide and iridium oxide have been studied extensively in this regard⁴. However, the high cost, low abundance and effects on the environment limit their large scale applications. In addition, rare earth oxides appear to be good supercapacitor materials. In particular, CeO₂ is expected to be a potential electrode material for supercapacitors, owing to its abundance across the earth, dynamic redox couple and eco-friendly features⁵. From the literature it can be seen that there are only few reports on the supercapacitor behavior of rare earth oxides. This is probably the first time that cerium oxide nano particles prepared via hydrothermal route are employed and examined as possible supercapacitor material. In the present work, we report and discuss a simple hydrothermal synthesis of CeO₂ nanoparticles for supercapacitor applications and the results obtained on the structural and electrochemical characterization studies carried out on this material.

Experimental

All of the reagents used in the present work were of analytical grade. 0.2 M of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was dissolved in 40 mL of water. 0.05 M of CTAB was added to the above solution. Ammonia solution was added drop wise to maintain the pH at 10 and the solution was stirred continuously for 2 h. A clear solution thus obtained was transferred to a Teflon-lined stainless steel autoclave and kept at 120 °C for 16 h. Finally, the solution was allowed to cool to room temperature. The precipitate formed following this process was washed with deionized water and ethanol several times. The end product was dried at 80 °C for 24 h and then it was annealed at different temperatures (300, 400, and 500 °C) for 1 h. Both the treatments were carried out in an atmosphere of air. The samples annealed at 300 °C are labeled as CeO_2 -300, while those annealed at 400 and 500 °C are labeled as CeO_2 -400 and CeO_2 -500 respectively. Electrochemical studies were made using CHI-660D electrochemical workstation. The working electrodes were prepared by mixing of 80% CeO_2 as the active material, 15% of activated carbon, 5% PTFE as the binder and few drops of ethanol was used as the solvent. 1 mg of the active material was pasted onto a graphite sheet substrate (1cm x 1cm). The prepared electrode was dried at 70 °C for 12 h. This was employed as the working electrode. 2M aqueous KOH was used as the electrolyte. The electrochemical measurements were carried out using three electrode cell configurations with CeO_2 as the working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode.

Results and discussion

XRD patterns of hydrothermally synthesized CeO_2 nanoparticles before and after heat treatment are shown in fig. 1. The crystalline nature of CeO_2 nanoparticles increases due to the increase of annealing temperature. The formation of CeO_2 in the cubic fluorite crystal structure could be identified from the XRD pattern and peak positions corresponds to (111), (220), (311), (400) agree with the JCPDS card no. 85-5923. Debye-Scherrer formula was used to calculate the average grain size of the sample.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{---(1)}$$

Where ' λ ' is the wavelength of the X-ray, ' β ' is the full width half maximum and ' θ ' is the diffraction angle. The average grain size was found to be 9.2, 9.8, 10.7, 11.6 nm for as prepared and annealed samples. This behavior of increasing crystallite size agrees well with the fact that at elevated temperature the nano particles exhibit a tendency to aggregate. The poor crystalline nature of the samples favors more charge transport at the electrode/electrolyte interface.

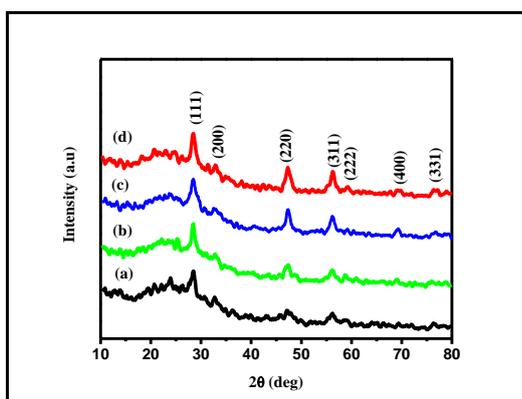


Fig.1. XRD pattern of CeO_2 a) as prepared, annealed at b) 300 °C, c) 400 °C and d) 500 °C

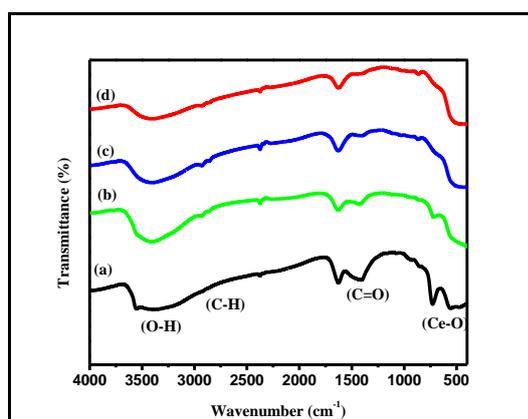


Fig.2. FTIR spectrum of CeO_2 a) as prepared, annealed at b) 300 °C, c) 400 °C and d) 500 °C

Fig. 2. represents the FTIR spectra of the CeO_2 nanoparticles prepared in the current work. The spectrum has absorption band at 2800–2900 cm^{-1} which is due to the C–H stretching mode of hydrocarbons. The band positioned at 2400 cm^{-1} was assigned for CO_2 adsorbed from air at the surface of CeO_2 ⁶. The absorption band at 1000–1300 cm^{-1} is assigned to the O–C and C–C bond vibrations⁷. The Ce–O stretching band around 450 cm^{-1} confirms the formation of CeO_2 nanoparticles⁸. FTIR spectra of all the samples exhibit bands around range of 3400 and 1625 cm^{-1} are attributable to the O–H vibrations. From these spectra it can be seen that the water

formation is almost removed on treatment at 600 °C. The diminishing strength of this absorption indicates removal of OH from the inner parts of the nano particle as the adsorbed water normally removed beyond 100 °C.

The SEM images of CeO₂ samples are shown in fig.3. This images are shows the presence of aggregated spherical nanoparticles. The well-defined aggregated nanoparticles facilitate easy access of OH⁻ ion from the bulk electrolyte solution and more ion diffusion through the active material which is essential for supercapacitor⁹.

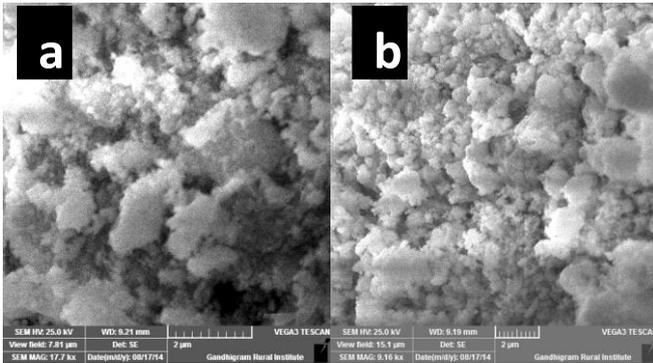


Fig.3. SEM images of CeO₂a) as prepared, annealed at b) 400 °C

The sample CeO₂-400(fig. 3b) was found to have distributed particles which facilitates to easy ion diffusion on the electrode/electrolyte interface.

Cyclicvoltammetry, galvanostatic charge–discharge, and electrochemical impedance analysis were carried out on the CeO₂ electrode materials. Fig. 4.shows the cyclicvoltammetric curves of the CeO₂ electrodes recorded at a scan rate of 5 mV s⁻¹. The quasi-rectangular shape of the CV curves indicates the pseudocapacitance nature of the CeO₂ electrodes.

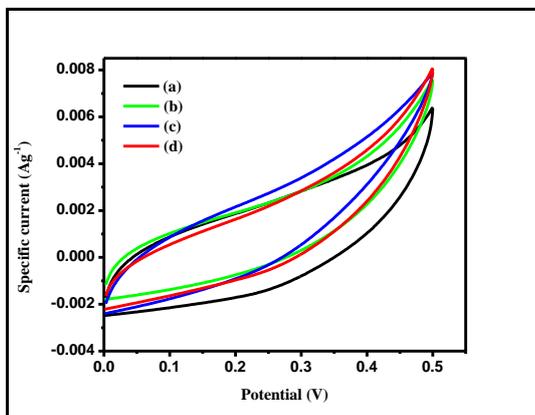


Fig.4. CV curve of CeO₂ electrodes at a scan rate of 5 mV s⁻¹ a) as prepared, annealed at b) 300 °C, c) 400 °C and d) 500 °C

From the CV curves, specific capacitance was calculated using the formula

$$C = \frac{Q}{m\Delta v} \text{-----(2)}$$

Where C is the specific capacitance (F g⁻¹); Q, the average charge during anodic and cathodic scan (C); m is the mass of the active material (g) and ΔV is the potential window (V). The specific capacitance values are 429, 441, 526, 459 corresponding to the electrodes as prepared, and the ones annealed at 300, 400 and 500 °C respectively at a scan rate of 5 mV s⁻¹ within a potential range of 0 to + 0.5 V. Samples annealed at 400 °C exhibit 23% increase in specific capacity over the as prepared sample. Fig. 5.shows the CV curves recorded at different scan rates for CeO₂-400 electrode. From fig.5 and 6, it is observed that the increase of scan rate leads

to a decrease in the specific capacitance, due to the electrode/electrolyte interface. At higher scan rates, the ions were intercalated probably only on the surface of the electrode, whereas at lower scan rate the ions could diffuse into the inner active sites as well, because lower scan rates provide larger lengths of time permitting better intercalation of the ions with the active sites¹⁰.

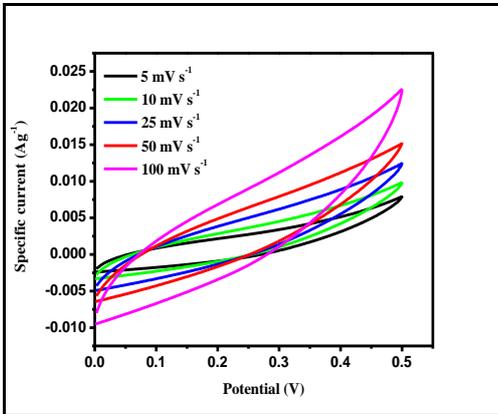


Fig.5. CV curves of a) CeO₂ – 400 °C electrode at different scan rates

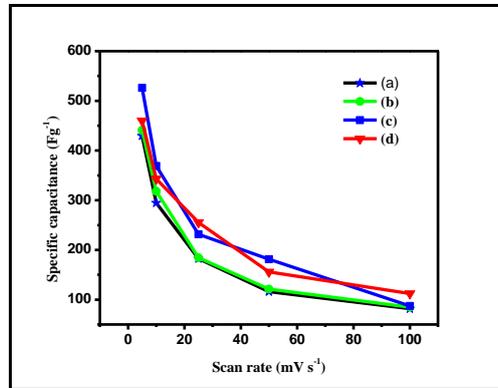


Fig.6. Scan rate versus specific capacitance of CeO₂a) as prepared, annealed at b) 300 °C, c) 400 °C and d) 500 °C electrodes

Galvanostatic charge-discharge curves of CeO₂ electrodes, recorded at a current of 2.5 A g⁻¹ within a potential window of 0.5 V are shown in fig. 7. The specific capacitance of the electrodes are calculated using the following equation

$$C = \frac{i\Delta t}{m\Delta v} \text{-----(3)}$$

Where C is the specific capacitance (F g⁻¹); i is the specific current (A); Δt is the discharge time (s); m is the mass of the active material (g) and ΔV is the potential window (V). The estimated specific capacitance values of CeO₂– as prepared, treated at 300, 400 and 500 °C respectively are 290, 340, 490, 435 F g⁻¹. Here again we could observe 70% enhancement in the specific capacitance. These results are similar those obtained from CV curves, indicating CeO₂–400 °C yields the better electrochemical performance for supercapacitor electrode material.

From fig. 8 and 9, it is seen that at low current densities, the ions have enough time to intercalate and deintercalate, thus the ions access the outer surface as well as the inner surface. But at high current densities, the ions access only the outer surface of the electrode leads to the decrease in specific capacitance¹¹.

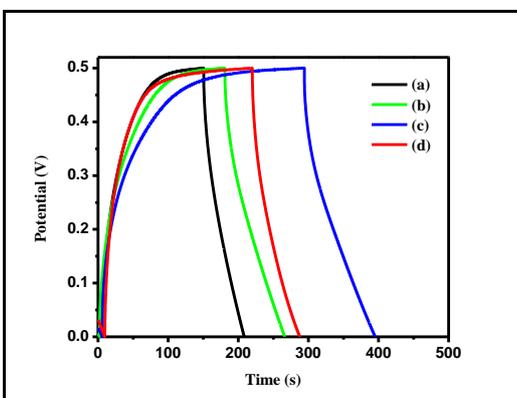


Fig.7. Charge discharge curves of CeO₂ electrodes at a specific current of 2.5 A g⁻¹ a) as prepared, annealed at b) 300 °C, c) 400 °C and d) 500 °C

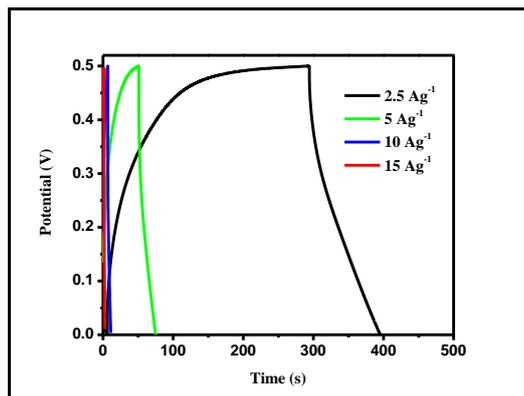


Fig.8. Charge discharge curve of CeO₂–400 electrode at different specific currents

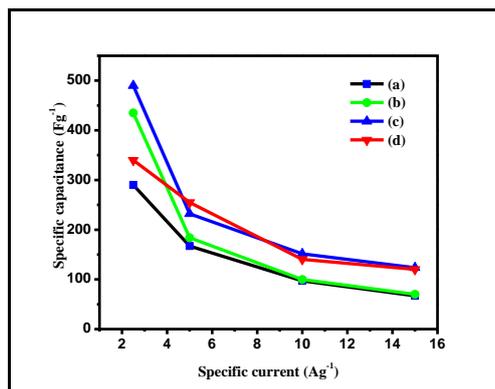


Fig.9. Specific current versus specific capacitance of a) as prepared, annealed at b) 300°C, c) 400°C and d) 500°C

Fig. 10 shows the electrochemical impedance measurement of CeO₂–400 electrode in the frequency range 0.01Hz - 100k Hz at the open circuit potential of 0.31V. The semicircle at the high frequency region corresponds to the charge transfer resistance, R_{ct} . This is related to the electro active surface area of the electrode, due to the faradic redox process of the CeO₂–400 electrode.

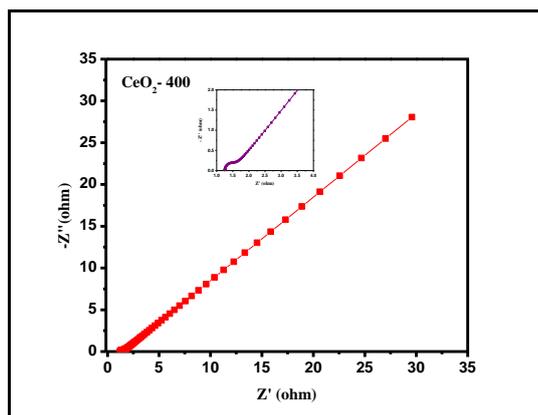


Fig.10. Nyquist plot of CeO₂–400°C electrode at 0.31 V

The R_{ct} value is 0.29 Ω for CeO₂–400. From this study, we could observe that CeO₂–400 has the lowest R_{ct} value. Hence, CeO₂–400 appears to be the best candidate for supercapacitor applications.

Conclusion

The CeO₂ nanoparticles have been synthesized by hydrothermal method. The cubic fluorite structure of CeO₂ was confirmed through XRD analysis. FTIR spectrum confirms the formation of Ce-O bonds. The CeO₂–400 electrode exhibits maximum specific capacitance of 526 F g⁻¹ with the charge transfer resistance of 0.29 Ω . High specific capacitance and low charge transfer resistance, make the CeO₂–400 electrode was optimally suited for supercapacitor applications.

References

1. Yi, W., Chun, X.G., Jiehua, L., Tao, C., Hongbin, Y., and Chang Ming, Li., Dalton Trans., 2011, 40, 6388–6391.
2. Wang, K., Huang, J., Wei, Z., J. Phys. Chem. C., 2010, 114, 8062–8067.
3. Simon, P., Gogotsi, Y., Nature Mater., 2008, 7, 845–854.
4. Xue, T., Xu, C. L., Zhao, D. D., Li, X. H., Li, H. L., J. Power Sources, 2007, 164, 953–958.
5. Ramchandra, S. K., Yong-Han, K. and Chan-Jin, P., IOP Nanotechnol., 2013, 24, 365401–365408.
6. Padmanathan, N. and Selladurai, S., RSC Adv., 2014, 4, 6534–6537.

7. Zhu, T., Chen, J. S. and (David) Lou, X. W.,J. Phys. Chem. C., 2011, 115, 9814–9820.
8. Goharshadi, E.K., Samiee, S., Nancarrow, P., J. Colloid and Interface Science., 2011, 356473–480.
9. Padmanathan, N., Selladurai, S., Ionics, 2014, 20, 409–420.
10. Nagamuthu, S., Vijayakumar, S., Muralidharan, G.,Energy Fuels, 2013, 27,3508–3515.
11. Vijayakumar, S., Nagamuthu, S., Muralidharan, G., ACS Sustain. Chem. Eng. 2013, 1, 1110–1118.
