

Cerium Oxide thin films as pH sensor Influence of deposition parameters, nanostructure morphology

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Abstract:

Nano structured cerium oxide thin films have been widely explored for miniaturized, solid state PH sensors owing to their high surface area, chemical stability and reactive oxygen vacancies, This paper presents the fabrication and characterization of nanostructured cerium oxide thin film ph sensing membranes using physical vapor deposition or solution based techniques, with emphasis on grain size, porosity, and surface termination. The nanostructures-such as nanocrystalline, nanorod ,or nanoparticle – embedded thin films-exhibit enhanced sensitivity and response time compared with bulk CeO₂ because of the increased density of surface OH groups and improved electrolyte-solid interface. Electrochemical and potentiometric measurements in standard buffer solutions show that the films display a linear potential response over a broad ph range (typically 2-12 with sensitivities approaching or exceeding the theoretical nernstian value (59 Mv/ph at 25 c) in optimally designed EIS OR ISFET type structures. The CeO₂ based membranes also demonstrate good selectivity against common ions, fast response/recovery times, and long-term stability under ambient and aqueous conditions, making them suitable for integration into microelectronic Ph sensors and biosensing platforms. This paper further discusses the influence of deposition parameters, nanostructure morphology , and doping (eg..with rare-earth elements) on the sensing performance ,highlighting routes to optimize hysteresis, drift, and temperature dependence. Overall, nanostructured cerium oxide thin films offer a facile, low-cost, and robust platform for developing high performance ph transducers for environmental, biomedical , and industrial monitoring applications.

Keywords: Nanostructured cerium oxide, PH sensor, Ion-sensitive field-effect transistor (ISFET), Electrolyte-insulator-semiconductor (EIS),Sensor.

Introduction

pH measurement is desired in many fields such as the medicine, food, agriculture, environment, etc. Several types of sensors are used for the pH measurement but the amperometric (limiting current) or potentiometric sensors are most commonly used [1-3]. Cerium Oxide (CeO₂) finds large number of applications due to unique properties like better electro-catalytic behavior, oxygen storage capacity and its transparent behavior for fabrication of optical biosensor [4-6]. Due to high diffusion coefficient for oxygen vacancy and good electronic-ionic conductor, Ceria is investigated as a gas sensing material by

many researchers [7, 8]. Cerium Oxide is chemically and thermally stable due to which it has attracted its usage in electrochemical fields [3]. The surface of cerium Oxide has large number of binding sites (up to 10^{16} cm^{-2}) which is favorable for achieving high pH sensitivity. This material is thermally stable and shows impenetrable behavior [3] in acid-base medium which makes it chemical stable against corrosion [3, 9]. It finds applications in photo-catalysis, data storage, carbon monoxide sensors, Ethanol Sensors, Hydrogen peroxide sensors, UV blocking systems, fuel cells[10-20]. Cerium Oxide has been reported [21-23] as pH sensing material but none of these reports has explored its applicability as sensing electrode over whole pH range (i.e. 1.0-14.0). Most of the previous reports [21, 23] have not measured response time while cerium oxide is used as sensing electrode. However Shuk et al [22] has stated that the response time of the ceria coated electrode around 1-2 minutes [22]. Hence, a sensing platform is required to overcome these limitations such as response time and wide pH range. Table 5.1 outlines the work carried out by various researchers on the Cerium Oxide material for its utilization as pH sensor.

Table 1: Comparison of work carried out on CeO₂ for pH sensing using several techniques.

S. N o.	Coating Technique Used	Response Measurement Technique Used				CeO ₂ film Thickness (nm)	Response time (s)	pH range	Solvents pH values used	Reference
1	Mass-modified technique	CV	Imp	-	-	20 μm	-	6-11	5.5-13.2	[21]
2	Hydrothermal synthesis	Emf response	-	-	-	0.3-0.5 mm	1-2 minute s	3-10	2-11	[22]
3	Sputtering	Cv	-	-	-	50 nm	-	2-12	2,4,6,8,10,12	[23]
4	e-beam evaporative	cv	LSV	Amp	-	400 nm	<15 s	1-14	1-14	Present work

*Amp: Amperometric, CV: capacitance-voltage, LSV: Linear Sweep Voltammetry, cv: cyclic voltammetry

As discussed in the Chapter 4, Ta₂O₅ based pH sensor [24] was fabricated which was suitable for sensing in the pH range of 1.0-12.0. Keeping the same spirit in view, the present chapter discusses the fabrication of electrochemical pH sensor based on CeO₂ thin film.

Materials and Methods

The thickness and coating parameters (Chamber pressure, degassing time, substrate temperature, degassing voltage etc.) were optimized prior to the fabrication of thin film. The optimized parameters were subsequently used to fabricate thin sensing layer on the selected bare electrodes. Thin films of CeO₂, characterized by high chemical stability and good electro-catalytic response, are evaporated on the glass substrates using E-beam coating technique. The sensing electrode, so fabricated, was characterized

using XRD, CCI and SEM for its structure and morphology. These coated electrodes are further investigated for pH sensing using electrochemical technique. Cerium Oxide pellets were procured from Umicore, Liechtenstein. Sodium hydroxide (NaOH) pellets and Hydrochloric acid (HCl, 35%) were procured from Merck, Germany. Thin films of CeO₂ were deposited on glass substrates using E-beam evaporation technique which is described in Section 2.2.3. In-situ thickness of the coating thin films was monitored using Quartz crystal thickness monitor (Intellimetrix) and further confirmed using a Reflectometer (F10-RT, Filmetrics, Germany) (See Section 2.3.2). XRD studies of the coated substrates were carried out using X-ray Diffractometer (D-8 Advance, Bruker, Germany) (See Section 2.3.1) to obtain information related to crystalline structure of sensing film. The properties of thin film such as surface morphology and roughness were investigated using FE-SEM (SU8010, Hitachi, Japan) (See Section 2.3.1), Coherence Correlation Interferometer (6000, Taylor Hobson, UK) (See Section 2.3.3). For pH sensing studies, resistance of electrodes were measured using source meter (4200, Keithley, USA). A pH meter (pico+, Lab India) was used to prepare the different solutions ranges from 1.0 – 14.0 using HCl and NaOH reagents. The adhesivity of the CeO₂coating on glass substrate was checked before and after interaction with acidic and basic medium. All the glassware used in this work autoclaved prior to use. The amperometric and linear sweep voltammetry measurements were performed using an electro chemical Work station (660C, CH Instruments, USA). pH of the tap water was measured with help of pH meter (LMMP-30, LABMAN, India).

Sensor Fabrication

CeO₂ was allowed to evaporate in the form of thin films on glass substrates using E- beam evaporation coating technique (Pfeiffer Vacuum, Model PLS 570 deposition system, Germany) discussed in Section 2.1.3 and were utilized as working electrode for electrochemical measurements. Prior to use, the glass substrates (1.5 x 1.0 mm), were cleaned thoroughly with acetone followed by ultra sonication. For coating, CeO₂ granules were placed in the Molybdenum boat and preheated for about 15 min to remove the impurities. Multifarious parameters such as chamber pressure, oxygen partial pressure, temperature of substrate, water flow rate were optimized and their values are presented in the Table 5.2. Thickness of the coating layer was maintained at 400 nm.

Table2: Process parameters for the coating of CeO₂ thin films

S. No.	Deposition Parameters	Values
1	Base Pressure	1x10 ⁻⁶ mbar
2	Oxygen Partial Pressure	2x10 ⁻⁴ mbar
3	Substrate Temperature	250° C
4	Substrate Rotation	20 RPM
5	Deposition rate	0.321 nm/sec

To fabricate the sensing membrane on the glass electrode, CeO₂ films of different thickness (300, 400,

500 and 600 nm) were prepared for further investigation of sensing. During these investigations, it was observed that the films thicker than 400nm had poor adhesion [25], while thinner films (thickness < 400 nm) yield inadequate response for the purpose of sensing. Hence, with CeO₂ film of thickness of 400 nm, were used for further investigations.

Results and Discussion

Structural Analysis

XRD studies were performed to study the crystalline structure of CeO₂ thin film and expedite the stability of physical and chemical nature of film before and after exposure in acidic as well as basic media. The XRD measurements support the crystalline structure of CeO₂ and also confirmed that the coating did not suffer any physical or chemical alteration while remaining in contact with electrolyte which is depicted in the Figure 5.1. The dominant peaks were found at 28.58°, 33.12°, 47.50° and 50.41° which are in accordance with previous reports [26-27] and corresponds to Bragg's diffraction from crystal planes defined by Miller indices (111), (200), (202) and (311) respectively. For XRD analysis of exposed electrodes, the one treated with most acidic (pH=1.0) and most alkaline (pH=14) solutions, were investigated. It was observed that, even after dipping for duration of 5 minutes, in these solutions, the coated CeO₂ film suffered neither chemical nor physical alteration.

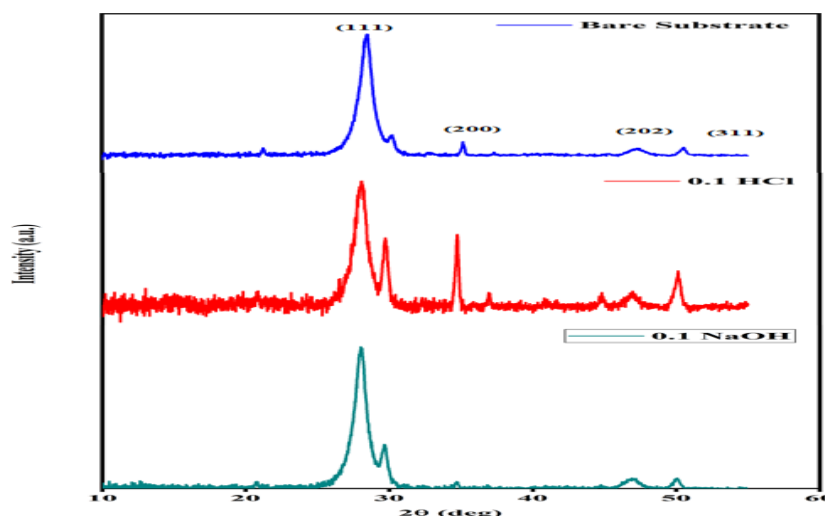


Figure 5.1: XRD data of bare CeO₂ thin films and after exposing them to harsh solvent (HCl) and alkaline medium

The average crystalline size (D) has been calculated by using Debye-Scherrer method by using Equation (5.1). s mean size of crystallites, λ is X-ray wavelength, K is crystallite shape factor which is equal to 0.9, β is full width at half maximum (FWHM) of diffraction peak. The crystallite size of bare, electrodes dipped in 0.1MNaOH and 0.1 MHCl is 175.7Å, 164.2Å and 169.4Å, respectively. The lattice constants are calculated and their values are found to be same in all the cases i.e. $a=b=c=5.40\text{Å}$ which are indicative of cubic or orthorhombic crystal structure. The crystal structure, lattice constants and crystal planes are also found to be same in all the cases, which indicates that the fabricated film is not affected, by any means, on interaction with chemical environment to which it is exposed,

Thickness Measurement

CeO₂ thin film thickness was also checked using a Reflectometer before and after their use in pH sensing studies. It was found that the thickness of CeO₂ thin film remains same before and after pH sensing studies in solutions of various pH which indicates that the material did not dissolve in the solutions during pH sensing studies. The XRD and thickness measurement reveal that the material retains its structure during the experiments in low as well as high pH solutions.

Roughness Estimation

CCI technique was used for the roughness measurement of the CeO₂ coated thin films and average variation in thickness was estimated to be about 0.2 nm. The surface map of the CeO₂ coated thin film yields thickness of 411 nm which is in good agreement, within 3%, of measurements yielded by thickness monitor. Even the thickness of the CeO₂ film, which was immersed in pH 1.0 solution for 15 minutes, indicates the same thickness as before its use as shown in the Table 5.3.

Table 3: Thickness measurement

pH used	Thickness of sensing layer (before dipping)	Thickness of sensing layer (after dipping)
1.0	399.8 nm	397 nm

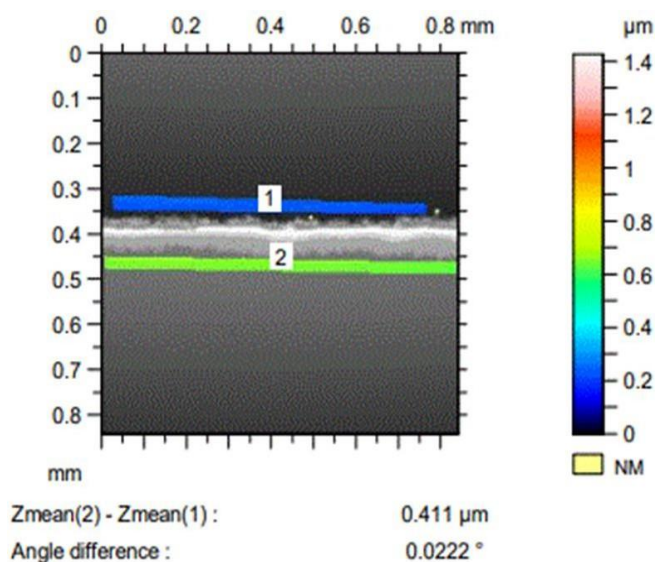
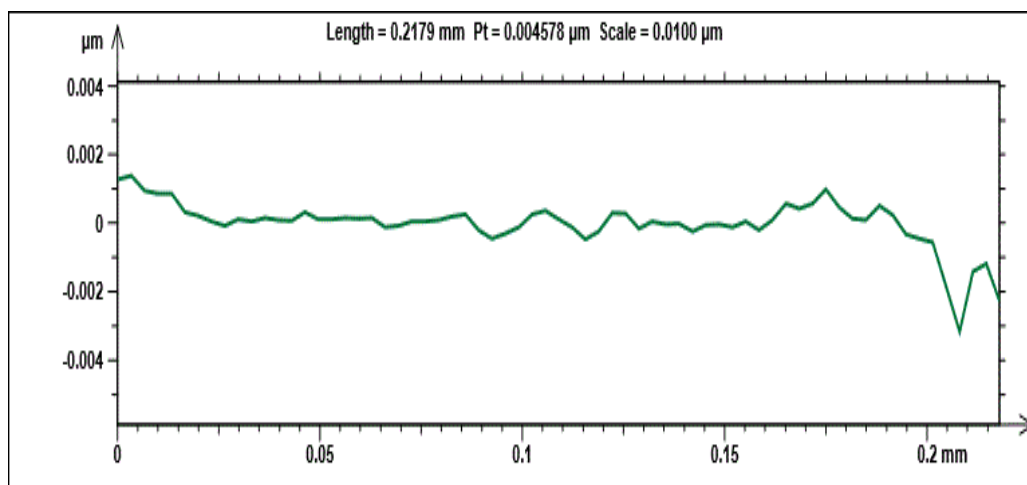


Figure2: CCI surface image and roughness plot of CeO₂ thin film.



Morphological Studies

Figure 5.3 (a, b) presents the 2-D surface morphology and cross-sectional view of the electrode material before sensing, while Figure 5.3 (c, d) presents the 2-D surface morphology and cross-sectional of electrode material after immersing it in 1.0 pH solution for 15m in. Figure 5.3(a) shows the star like structure of CeO₂ films. Figure 5.3(c) confirms that the material retained its star like structure after its treatment. Film thickness of the electrode material was also estimated using cross-sectional surface micrographs [see Figure 5.3(b,d)] and found to be approximately 400nm, which again confirms that the electrode material did not dissolve in the solution during the study and remains stable.

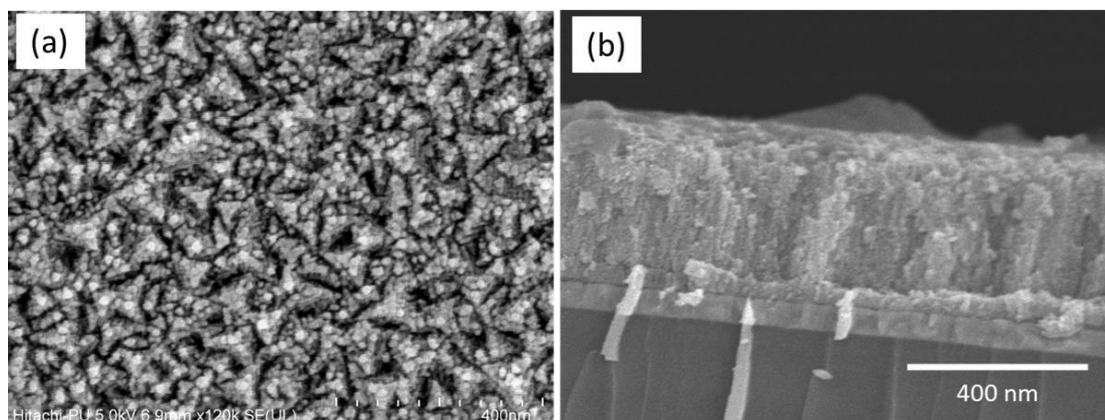


Figure 5.3: (a) SEM image of bare CeO₂ thin film and (b) Cross-sectional SEM image of bare CeO₂ thin film

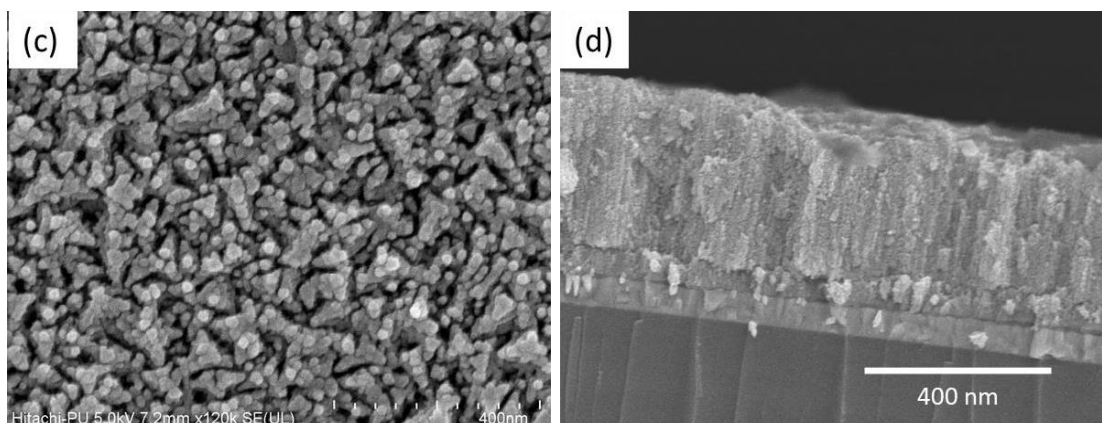


Figure 5.3: (c) SEM image of used CeO₂ thin film and (d) Cross-sectional SEM image of used CeO₂ thin film

Sensing mechanism

pH sensing occurs through a mechanism as ceria membrane interacts with electrolytic solution in the hydrolysis of surface due to proton exchange process at the interface. This interaction of solid membrane with liquid results into the hydrolysis of surface which results into the initiation of proton exchange process at the interface. The coated material will either accept the protons or donate them during the above reactions. The sensing process is therefore regulated by the above mechanisms and the resistance results from a change in the hydronic ion concentration in the solution. The thin film surface will have zero charges or point of zero charges before applying the voltage (pH_{zc}). When the electrolyte pH reaches pH_{zc}, leading to more negative ion (O⁻) formation, the CeO₂ coated surface becomes negative. Hence, it would also favor an acidic nature. When the pH of the electrolyte is less than pH_{zc}, a vice versa phenomenon can be explained. Whereas, the solution will be recognized as neutral when the OH⁻ ions present in the solution are equal to pH_{zc} [28].

Sensing Studies The sensitivity of electrode material was studied by using amperometry and linear sweep voltammetry techniques employed using different pH solutions. The response time of the sensing electrode was measured by using amperometry in which current was recorded as a function of time. The presence of electro-catalytic active species was confirmed by performing Linear Sweep voltammetry on CeO₂ coated glass electrodes, Pt electrode and Ag/AgCl were used as the working, counter and reference electrodes respectively. Various solutions with pH ranging from 1.0 to 14.0 were used as electrolyte and current was recorded as a function of time and potential. The results of these investigations are discussed below:

Response time of Electrode Amperometric studies were performed on CeO₂ coated electrodes to estimate the response time of electrolytes in different pH. Figure 5.4 shows the time variation of current for coated electrodes immersed in solutions of different pH for a fixed duration of 120 seconds, when constant voltage of 0.5 V was applied.

Response time of Electrode

Amperometric studies were performed on CeO₂ coated electrodes to estimate the response time of electrolytes in different pH. Figure 5.4 shows the time variation of current for coated electrodes immersed in solutions of different pH for a fixed duration of 120 seconds, when constant voltage of 0.5 V was applied.

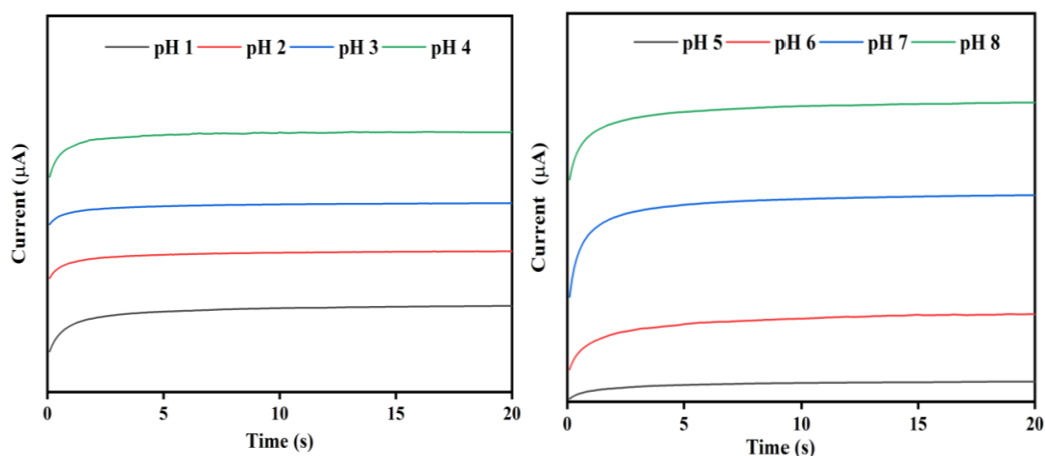
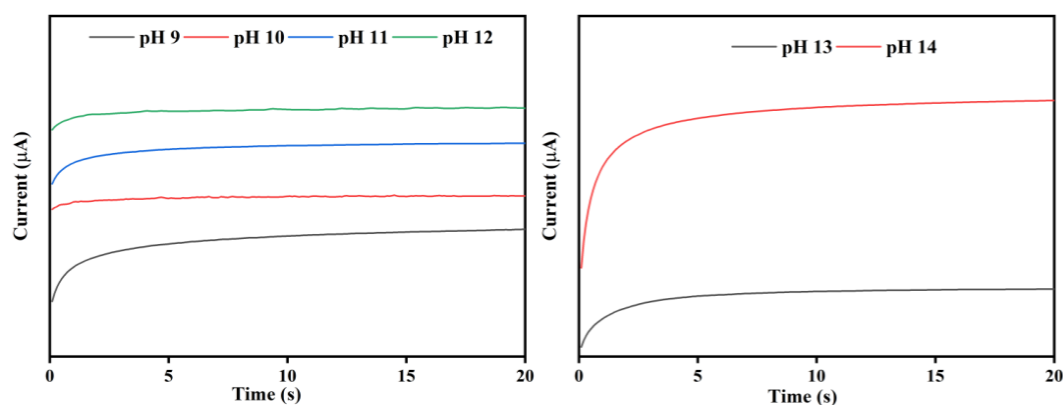


Figure 4: Current response of coated electrodes in different pH electrolytes (1.0-14.0).



From these curves, it is evident that the signal stabilizes within few seconds and it remains stable upto 2 minutes for exposure in all solutions. The response time of each electrode was observed to be less than 15 seconds. In alkaline solutions (pH 8.0 - 14.0), it is observed that it takes more time to get stabilized. The signal is more drifted in case of high alkaline solutions such as pH=13.0 and pH =14.0. The experiments were repeated three times with fresh solutions and freshly prepared electrode. A consistent response of the coating material was observed. These results confirm the electro-catalytic activity of the coated substrates.

Linear Sweep Voltammetry (LSV)

In this study, current is measured as a function of applied voltage, which is scanned over the range -0.5 V to 0.5 V. The linear sweep voltammetry curves at different pH values were obtained at a constant scan rate and are shown in the Figure 5.5. The saturation current was found to be a function of pH of the solution. This change in current confirms the presence of electro-catalytic active species in the solution and a commendable electro-catalytic activity in the range $1.0 \leq \text{pH} \leq 14.0$.

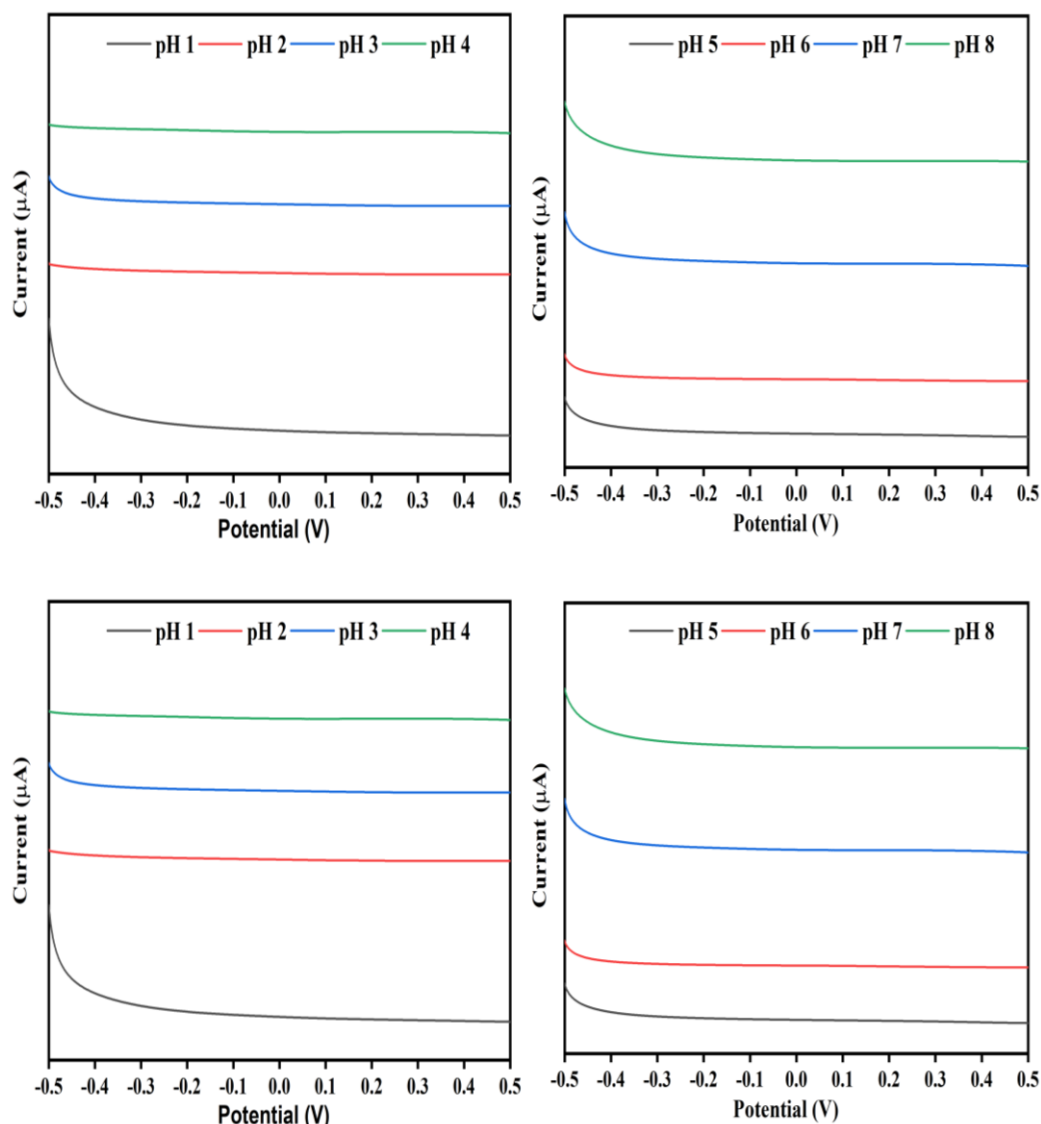


Figure 5.5: LSV curves of coated substrates in different pH range of 1.0-14.0

Cyclic Voltammetry Studies

Cyclic Voltammetry is used to study the oxidation and reduction process of the electroactive species present in the electrolyte and the results obtained in the graphical form is known as cyclic voltammograms. The graph is plotted against two parameters i.e. on x-axis in terms of potential and current on y-axis and is shown in the Figure

5.6. In this work, cyclic voltammetry is used to investigate the coated material stability. Various electrolytes of different pH were used to perform the stability test.

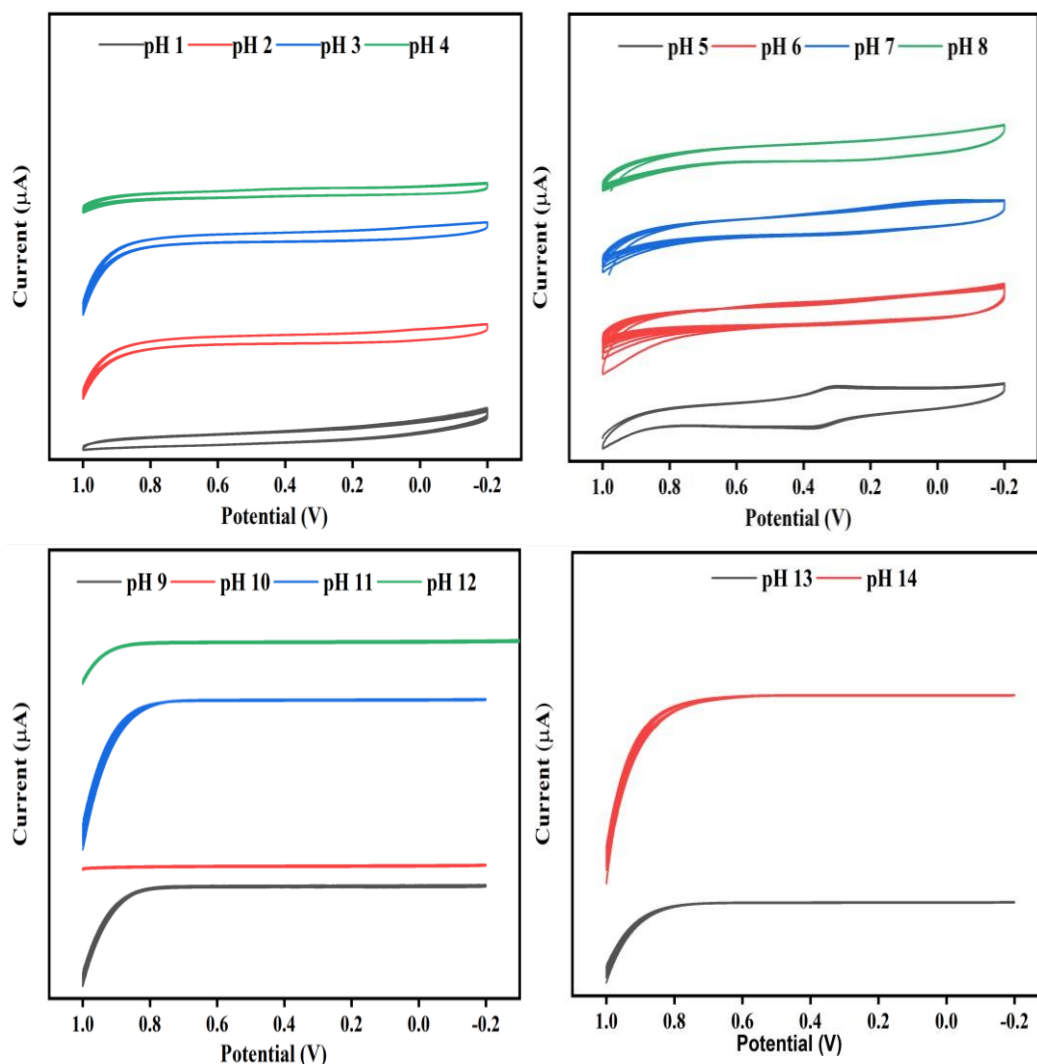


Figure 5.6: Cyclic Voltammograms of coated substrates in 1.0-14.0 pH solutions

Applications

Solutions of different pH values were prepared and the electrodes were dipped. After dipping, the response of the electrodes was measured in terms of resistance by using Source Meter. It is observed that the resistance of the electrodes increases in the range

$1.0 \leq \text{pH} \leq 6.0$ from 0.10 to 0.40 MΩ. At pH 7.0, decrease in resistance was observed reaching the lowest resistance value 0.09 MΩ. The resistance values in alkaline solutions are higher than in acidic solutions. A steady but slow decrease was found in

The resistance upon using the further pH range i.e. 8.0-14.0 pH solutions. The precision of the pH sensor was also estimated during this technique which is shown in the Table 5.4. All the measurements were repeated three times and the consistent results show the precision of pH sensor measurements.

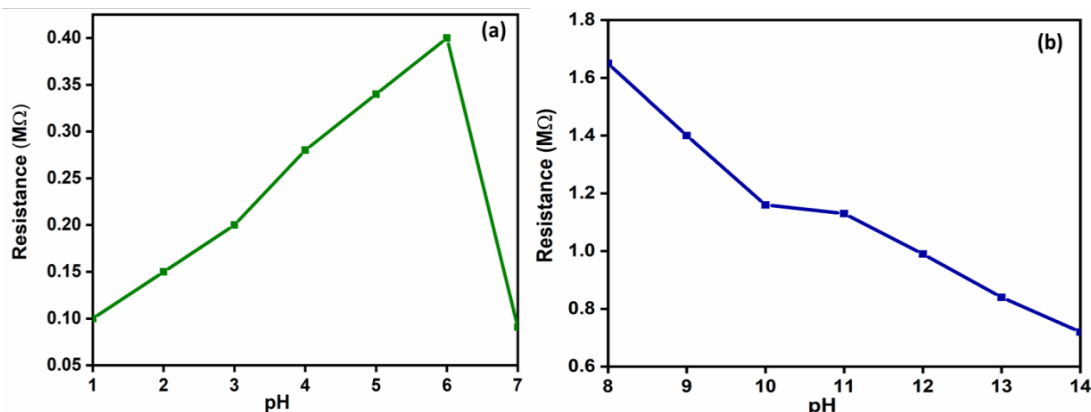


Figure5.7: Effect of the pH on the resistance of coated electrodes

Table 5.4: Resistance measurements of coated electrodes

pH	Resistance(MΩ)			Average Resistance(MΩ)
	R1	R2	R3	
1	0.11	0.09	0.10	0.10
2	0.15	0.13	0.17	0.15
3	0.20	0.19	0.22	0.20
4	0.28	0.26	0.30	0.28
5	0.33	0.34	0.35	0.34
6	0.40	0.41	0.39	0.40
7	0.09	0.095	0.087	0.091
8	1.65	1.68	1.62	1.65
9	1.40	1.38	1.42	1.40
10	1.16	1.12	1.20	1.16
11	1.13	1.14	1.12	1.13
12	0.99	0.92	1.06	0.99
13	0.84	0.80	0.88	0.84
14	0.72	0.68	0.76	0.72

Reliability of sensors with Tap water

The CeO₂ thin film-based sensors was tested with ordinary water samples using the above methods i.e. amperometric, linear sweep voltammetry and cyclic voltammetry. A range of controlled pH samples were used to investigated to validate the reliability of sensors and the results are presented in Figure 5.8 (a-c). After comparison of these findings with the above reported results, it can be concluded that the

presence of other ions does not influence the performance of CeO₂based sensor.

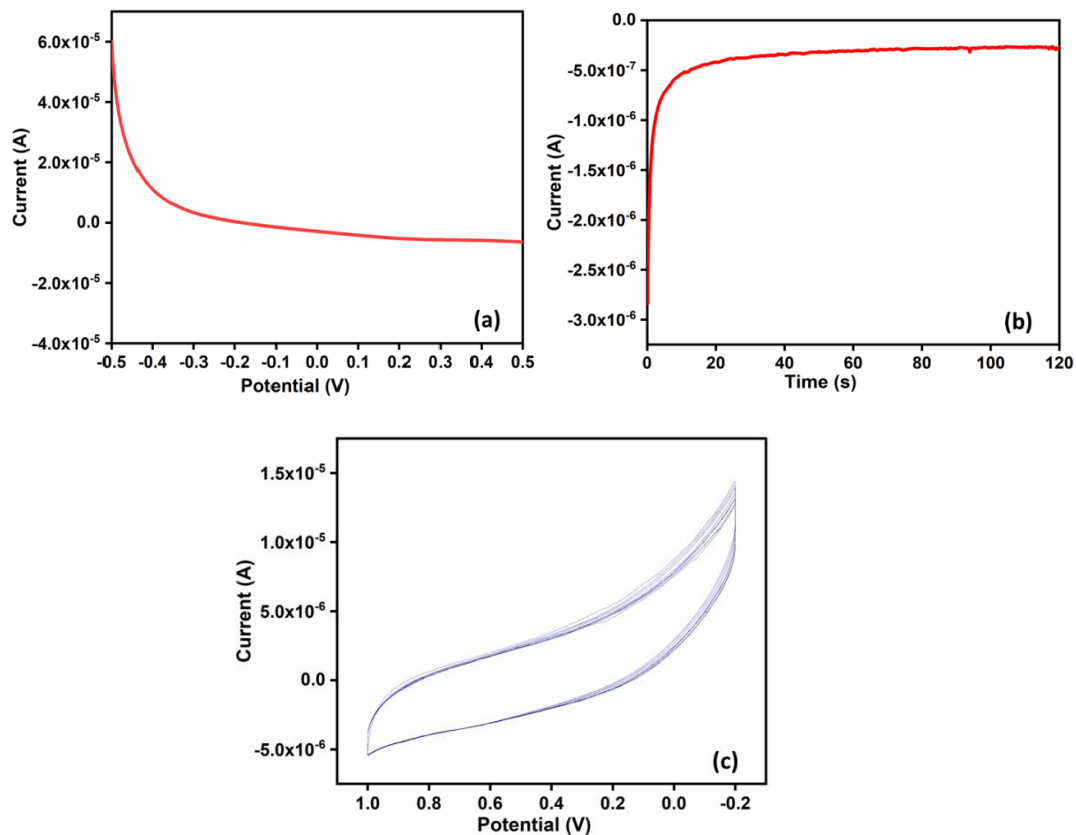


**Figure 5.8: (a) Linear sweep Voltammetry Graph
(b) Time Response and (c) Cyclic Voltammogram of Tap Water**

Error Analysis

Water samples were taken from different sources and their pH was measured using the fabricated sensor and a standard pH measuring device. The values were compared and are shown in Table-5.5. The result of sensor agrees with the measurements by pH meter with in 3%.

Table 5.5: Comparisons of pH values using CeO₂/glass electrode and a pH meter on water samples collected from different sources.

S. No.	pH measurements using CeO ₂ /glass electrode	pH measurements using pH meter	% error
1	7.70	7.57	1.71
2	6.80	7.00	2.85
3	7.30	7.16	1.95
4	6.90	6.81	1.32
5	7.40	7.53	1.72

Conclusion

The values were compared and are shown in Table-5.5. The result of sensor agrees with the measurements by pH meter with in 3%.

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Conflict of Interest: Author has no conflict of interest .

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