CHAPTER – V

Loading of RuO$_2$ on Nanostructured TiO$_2$ Thin Films and Their Supercapacitor Behavior
5. Introduction

It is well known that, the supercapacitance is primly surface phenomenon and not the bulk [1-4]. Therefore, effectively cost can be lowered by utilizing less ruthenium oxide content, just by loading onto the other low cost matrix of nanostructured material. This will be results into effective utilization of ruthenium and provides high surface area along with attainability of high capacitance [5, 7]. Nanostructured TiO$_2$ having great interest in industrial due to its high surface area. Recent reports on dye sensitized solar cell reveled that, TiO$_2$ is semiconducting material having suitable band position with the electrolyte [8]. In order to improve the electroactive surface area (ESA) by utilization of small amount of ruthenium oxide may lead to enhancement in capacitance.

One-dimensional (1D) semiconductor nanostructures have attracted considerable research attention because of their great potential for fundamental research and technological applications [9]. A TiO$_2$ nanoparticle films on a transparent conducting oxide electrode is typically employed to be the anode of the DSSCs. A recorded solar light-to-current conversion efficiency of the DSSCs more than 10% is achieved using this high surface-area photoanode [8]. The large capacitance exhibited by the systems has been confirmed, it arise from a combination of the double layer capacitance and pseudocapacitance associated with the participation of adsorbed intermediate in the surface redox type reaction. The double layer capacitance belong with the surface area, no charge transfer across the surface take place and pseudocapacitive behavior is observed when adsorbed intermediats are involved during the course of faradiac reaction [10-11].

From the conclusion of chapter III SILAR synthesized RuO$_2$ exhibits a higher capacitance. Accordingly, the SILAR method is used to load RuO$_2$ on the different nanostructured TiO$_2$ thin films synthesized by chemical methods.
SECTION (I)
Loading of RuO$_2$ on nanostructured TiO$_2$ thin films by chemical methods

5.A Loading of RuO$_2$ on TiO$_2$ nanoparticles by SILAR method

Keeping above concept in mind, the approach is utilized to improve the capacitive performance by enhancing the surface area with utilization of RuO$_2$ material; hence TiO$_2$ nanoparticles are decorated by loading RuO$_2$ material, where TiO$_2$ nanoparticles may offer a large surface area and adsorbed RuO$_2$ may contribute for pseudocapacitance.

5.A.1 Experimental details

5.A.1.1 Loading of RuO$_2$ on to the TiO$_2$ nanoparticles electrode

TiO$_2$ nanoparticles were synthesized by adopting a SILAR method. The detail of synthesis process is discussed in the chapter IV, section 4.A. RuO$_2$ loaded on the predeposited TiO$_2$ nanoparticles by using SILAR method. The detail synthesis procedure of RuO$_2$ is given in the chapter III, section 3.B. The deposition of RuO$_2$ by SILAR method is carried out on the stainless steel and predeposited TiO$_2$ nanoparticle (on stainless steel substrate). The prepared films further characterized for their optical, electrical, morphological and wettability studies.

5.A.1.2 Characterization techniques

TiO$_2$ nanoparticles are synthesized using SILAR method and RuO$_2$ is loaded on to using SILAR method. The synthesized films were characterized by using various techniques in order to get information about the structural, surface morphological, electrical, optical and wettability properties.

5.A.2 Results and discussion

5.A.2.1 Thickness measurement

Fig. 5.1 (a) shows the graph of weight of RuO$_2$ deposited on TiO$_2$ film with number of deposition cycles and (b) shows photograph of the RuO$_2$ loaded on TiO$_2$ film. The film thickness was found to be increased with deposition cycles and remained constant after 100 cycles. The rate of
increase in thickness was not constant. The rate of RuO₂ deposition is higher on the TiO₂ surface as compared to the stainless substrate; attributed to the TiO₂ nanoparticles provide more nucleation sites to deposit the RuO₂ material.

**Fig. 5.1** (a) Variation of RuO₂ film thickness with deposition cycles on different substrate. Fig. (b) Shows the photograph of the RuO₂ loaded on TiO₂ nanoparticle thin film.

### 5.A.2.2 Structural characterization

Film crystallinity was analyzed by using X-ray diffraction technique. The XRD patterns of RuO₂ loaded on the TiO₂ (on stainless steel substrate) is shown in fig 5.2. The XRD pattern of film shows no well-defined diffraction peaks of RuO₂ (on steel substrate), indicating that ruthenium oxide is amorphous on amorphous TiO₂ surface. The amorphous phase is obtained which is reasonable for supercapacitor application [12].
Fig. 5.2 X-ray diffractogram of RuO$_2$ loaded on TiO$_2$ nanoparticle thin films on stainless steel substrate.

5.A.2.3 FT-IR study

Fig. 5.3 shows FT-IR spectrum of the RuO$_2$ loaded on TiO$_2$ nanoparticles. From this spectrum, it can be observed apparently that strong band ($\nu_1$) at around 560 cm$^{-1}$ is associated with the characteristic stretching mode of RuO$_2$ [13]. The absorption peak ($\nu_2$) at around 620 cm$^{-1}$ is assigned to characteristic stretching of TiO$_2$. The absorption peak at 1638 cm$^{-1}$ may be due to the bending vibration of hydroxyl groups of molecular water ($\nu_3$). The absorption at 3391 cm$^{-1}$ indicates that the presence of hydroxide group ($\nu_4$). In results we found that the different phase formation of RuO$_2$ and TiO$_2$ materials, while TiO$_2$ absorption band shows absorption as compared to RuO$_2$ band ascribed to the large content of TiO$_2$ material.
5.A.2.4 Surface morphology

The two-dimensional surface morphological study of the RuO$_2$ loaded on TiO$_2$ nanoparticles has been carried out from SEM image. Fig. 5.4 shows the SEM images of RuO$_2$ loaded on TiO$_2$ nanoparticles thin film on the stainless steel substrate at different magnifications X5,000 and X100,000. The morphology shows that the substrate is well covered with RuO$_2$ nanoparticles. From the fig. 5.4 (a), one can see the spherical grain morphology of RuO$_2$ favored on the TiO$_2$ surface with porous structure. At higher magnification smooth and fine features of RuO$_2$.nH$_2$O material is observed (fig. 5.4 (b)). A smooth surface with fine features frequently indicates as amorphous or nanocrystalline structure. Uneven grain size was observed on the surface is due to the rough surface of TiO$_2$ nanoparticles.
5. A. 2. 5 Optical absorption study

Fig. 5.5 (a) shows optical absorption spectra for TiO$_2$ and RuO$_2$ loaded TiO$_2$ thin films. The optical absorption spectra elucidate that the TiO$_2$ film was highly transparent; however after loading of RuO$_2$, drastic and considerable absorption increase in visible region was noticed. Increase in the absorption coefficient is observed after loading of RuO$_2$. Fig. 5.5 (b) shows the presence of the direct optical transition. From the graph, for RuO$_2$ loaded on TiO$_2$ nanoparticles, the band gap value of 2.65 eV was obtained. However, bare RuO$_2$ prepared by SILAR method exhibits a band gap 2.08 eV. Such type of increase in band gap (blue shift) after loading on TiO$_2$ nanoparticles due to the wide band gap material composed with low band gap material [14, 15].

Fig. 5.4 The SEM micrographs of RuO$_2$ loaded on TiO$_2$ nanoparticles at (a) (X5,000) and (b) (X100,000) magnifications.
Fig. 5.5 (a) shows variation of absorption ($\alpha$) with wavelength ($\lambda$) of TiO$_2$ and RuO$_2$ loaded TiO$_2$ thin films on glass substrates. (b) Plots of ($\alpha$hv)$^2$ vs. energy hv of TiO$_2$ nanoparticles and RuO$_2$ loaded on TiO$_2$ nanoparticles.

5.A.2.6 Electrical resistivity

From fig. 5.6, it is clearly seen that both TiO$_2$ and RuO$_2$ loaded films shows negative temperature coefficient of resistance, i.e. resistivity decreases with increase in temperature, which attributed to semiconducting nature of thin films. After loading of RuO$_2$ on TiO$_2$ film, the electrical resistivity was decreased from $10^5$ to $10^4$ $\Omega$.cm. This decrease in electrical resistivity of RuO$_2$ loaded TiO$_2$ film is due to the incorporation of RuO$_2$ material.

Fig. 5.6 The variation of electrical resistivity (log $\rho$) with temperature (1000/T) of TiO$_2$ and RuO$_2$ loaded TiO$_2$ films.
5.A.2.7 Contact angle measurement

Fig. 5.7 (a) and (b) shows the measurement of contact angles for TiO$_2$ nanoparticles and RuO$_2$ loaded TiO$_2$ thin films and were found to be 61$^\circ$ and 14$^\circ$, respectively. Decrease in contact angle after loading of hydrous RuO$_2$ is due to the surface hydroxyle bonds [16, 17]. The contact angle factor is known to affect the wettability of a solid surface greatly.

![Fig. 5.7 Measurement of water contact angles for (a) TiO$_2$ nanoparticles and (b) RuO$_2$ loaded TiO$_2$ thin films.](image)

5.A.3 Summary and conclusions

In summery, SILAR method is successfully employed for the loading of RuO$_2$ material on the surface of TiO$_2$ nanoparticles. The XRD pattern shows formation of amorphous RuO$_2$ on the surface of TiO$_2$ nanoparticles. FT-IR spectrum shows hydrous RuO$_2$ loaded on TiO$_2$ surface. The SEM shows increment in particle size of the RuO$_2$ particle after loading on to TiO$_2$ nanoparticles. Room temperature resistivity and optical band gap shows the semiconductor nature of the electrode with 2.65 eV band gap. Superhydrophilic nature of the electrode surface may contribute in the supercapacitor property. In order to enhance the capacitive property, RuO$_2$ productively loaded on the TiO$_2$ nanoparticles.
5.B Loading of RuO$_2$ on TiO$_2$ nanoflakes by SILAR method

As a supercapacitive electrode, besides the electronic conductivity, the morphology of nanostructure film plays a vital role in enhancing electroactive surface area (ESA) [18-20]. So as to, besides resistive TiO$_2$, to enhance the ESA, RuO$_2$ is loaded on the TiO$_2$ nanoflower. Therefore, the approach is to improve the capacitive performance by enhancing the surface area and utilization of RuO$_2$ material. The RuO$_2$ material is loaded on the TiO$_2$ nanoflowers consisting homocentrically grown nanoflakes.

5.B.1 Experimental details

5.B.1.1 Loading of RuO$_2$ on the TiO$_2$ nanoflake electrode

TiO$_2$ nanoflakes were synthesized by CBD method. Synthesis process in details is discussed in the chapter IV, section 4.B. RuO$_2$·nH$_2$O weighed down on the predeposited TiO$_2$ nanoflakes by using SILAR method. The detail procedure of RuO$_2$ deposition is given in the chapter III, section 3.B. The deposition of RuO$_2$ material by SILAR method is carried out on the stainless steel and predeposited TiO$_2$ nanoflakes thin films.

5.B.1.2 Characterization techniques

The RuO$_2$ loaded TiO$_2$ nanoflakes films were characterized for structural, surface morphological, electrical, optical properties and wettability using the techniques described in section 3.A.1.3.

5.B.2 Results and discussion

5.B.2.1 Thickness measurement

Fig. 5.8 (a) shows the graph of weight of RuO$_2$ deposited on TiO$_2$ film with deposition cycles and (b) shows photograph of the RuO$_2$ loaded on TiO$_2$ film. The film thickness was found to be increased with deposition cycle and remained constant after 100 cycles. The rate of increase in thickness was not constant. The rate of increase in deposited weight of RuO$_2$ on the TiO$_2$ surface is larger as compared to the stainless substrate.
Fig. 5.8 (a) Variation of weight deposited of RuO$_2$ film with deposition cycles on different substrates. Fig. (b) shows the photograph of the RuO$_2$ loaded on TiO$_2$ nanoflakes.

5.B.2.2 Structural characterization

The XRD patterns of RuO$_2$ loaded on the TiO$_2$ stainless steel substrate is shown in fig 5.9 (a). Fig. 5.9 shows XRD pattern of RuO$_2$ thin films, no well-defined diffraction peaks other than steel substrate, indicating that RuO$_2$ films are amorphous on TiO$_2$ surface.

Fig. 5.9 X-ray diffractogram of RuO$_2$ loaded on TiO$_2$ nanoflake thin films on stainless steel substrate.
5.B.2.3 FT-IR study

The FT-IR absorption spectrum of RuO$_2$ loaded on TiO$_2$ thin films in the range 4000–400 cm$^{-1}$ are shown in fig. 5.10. The four sharp absorption bands at $v_1$: 612, $v_2$: 800, $v_3$: 1631 and $v_4$: 3403 cm$^{-1}$ are attributed to the stretching vibration of TiO$_2$ in anatase, shoulder edge band of RuO$_2$ [13], peroxo group, vibration of hydroxyl groups of molecular water and stretching vibrations of OH, respectively. Shoulder edge band of RuO$_2$ is very smaller (shoulder edge band is very weak band) in context with the TiO$_2$ strong band. This result specifies that, the content of TiO$_2$ is larger than RuO$_2$.

![FT-IR spectrum](image)

**Fig. 5.10** FT-IR spectrum of RuO$_2$ loaded on TiO$_2$ nanoflakes.

5.B.2.4 Surface morphology

The two-dimensional surface morphological study of the RuO$_2$ loaded on TiO$_2$ nanoflakes has been carried out from SEM image. Fig. 5.11 shows the SEM image of RuO$_2$ loaded on TiO$_2$ nanoflakes thin film at different magnifications X10,000 and X50,000. The fig. 5.11 (a) shows film consists of TiO$_2$ nanoflakes and fine features of RuO$_2$ material. At higher magnification, fig. 5.11 (b) shows SEM image at X50,000, in the pores between TiO$_2$ nanoflakes a fine features of RuO$_2$ is deposited.
Fig. 5.11 SEM micrographs of RuO$_2$ loaded on TiO$_2$ nanoflakes at (a) X10,000 and (b) X50,000 magnifications.

5.A.2.5 Optical absorption study

Fig. 5.12 (a) shows optical absorption spectra for TiO$_2$ and RuO$_2$ loaded TiO$_2$ thin films. A careful study of both spectra shows only one edge (400 nm) for TiO$_2$ thin films, whereas RuO$_2$ loaded TiO$_2$ film shows two absorption edges (400 and 490 nm). The fundamental edges for TiO$_2$ and RuO$_2$ material are found to be strongly dependent on photon energy, indicating presence of more than one transition for given coupled semiconductor system [21]. For RuO$_2$ very sharp edge is not observed, due to the amalgamation of RuO$_2$ in the pores of the TiO$_2$. This result is attributed to existence of separate transitions for TiO$_2$ and RuO$_2$ thin films since, if they form composite or mixed phase then possesses one and same transition. RuO$_2$ is loaded on TiO$_2$ thin films like a dye adsorbed on TiO$_2$ in DSSC’s [22]. From the graph fig. 5.12 (b), for RuO$_2$ loaded on TiO$_2$ nanoflakes, the band gap value of 2.45 eV was obtained.
Fig. 5.12 (a) shows variation of absorption ($\alpha t$) with wavelength ($\lambda$) of TiO$_2$ and RuO$_2$ loaded TiO$_2$ thin films on glass substrates. (b) Plots of $(\alpha h\nu)^2$ vs. energy $h\nu$ of TiO$_2$ and RuO$_2$ loaded on TiO$_2$ nanoflakes thin film.

5.B.2.6 Electrical resistivity

Fig. 5.13 shows the variation of the dark resistivity with temperature. It is observed that the resistivity of films was decreased with increase in temperature, indicating a semiconducting electrical behavior. A room temperature electrical resistivity of TiO$_2$ and RuO$_2$ loaded TiO$_2$ was of the order of $10^4$ and $10^3$ Ω.cm, respectively.

Fig. 5.13 The variation of dark electrical resistivity ($\log \rho$) with temperature ($1000/T$) of TiO$_2$ and RuO$_2$ loaded TiO$_2$ films.
5.2.7 Contact angle measurement

Fig. 5.14 (a) and (b) shows the measurement of contact angles for TiO$_2$ nanoflakes and RuO$_2$ loaded TiO$_2$ thin films and were found to be 46$^\circ$ and 20$^\circ$, respectively. Decrease in contact angle after loading of hydrous RuO$_2$ is due to the hydroxyl bonds on RuO$_2$ surface [23]. The contact angle factor is known to affect the wettability of a solid surface greatly.

![Fig. 5.14 Measurement of water contact angle for (a) TiO$_2$ nanoflakes and (b) RuO$_2$ loaded TiO$_2$ thin films.](image)

5.1B.3 Summary and conclusions

In summary, SILAR method is successfully employed to the loading of RuO$_2$ on the surface of TiO$_2$ nanoflakes. XRD pattern shows the formation of amorphous RuO$_2$ on the surface of TiO$_2$ nanoflakes. FT-IR study confirms the formation of hydrous RuO$_2$ on the surface of the TiO$_2$ nanoflakes. The SEM shows total coverage of TiO$_2$ nanoflake by RuO$_2$ particles. Room temperature resistivity and optical band gap shows the semiconductor nature of the electrode with 2.45 eV band gap. Superhydrophilic nature of the electrode surface may contribute in the supercapacitor property. In order to enhance the capacitive property, RuO$_2$ is competently loaded on the TiO$_2$ nanoflakes.
Section II

Supercapacitive behavior of the RuO$_2$ loaded nanostructured TiO$_2$ thin films

5.C Introduction

Hydrous ruthenium dioxide (RuO$_2$.nH$_2$O) is the most promising electrode material for supercapacitors due to its intrinsic reversibility of surface redox couples and ultrahigh pseudocapacitance [24-27]. Since the superficial redox transitions of RuO$_2$ involve a proton–electron double injecting/expelling process. Such excellent performances, unfortunately, cannot be maintained for relatively thick RuO$_2$.nH$_2$O films, especially the high-power application. This phenomenon is commonly found for most electroactive materials, due to longer diffusion lengths of ions/electrons. Thus, three-dimensional (3D), mesoporous, ordered/a periodic architectures are desirable for improving such an issue. Four steps were proposed to determine the capacitive performance of RuO$_2$.nH$_2$O: (i) electron hopping within RuO$_2$.nH$_2$O particles; (ii) electron hopping between particles; (iii) electron hopping between electrode materials and current collectors; and (IV) the proton diffusion within RuO$_2$.nH$_2$O particles [28]. The intraparticle electron-hopping resistance of RuO$_2$.nH$_2$O particles can be reduced by loading on stable metal oxide while it results in an increase in the diffusion barrier of proton within crystalline RuO$_2$ and a loss of active sites [29].

The degradation aspects may be exacerbated due to the possible electrochemical abuse resulting from possible overcharge and over discharge during their sustained operation. In this context, hydrous ruthenium oxide attached on TiO$_2$ is expected to be more useful due to their enhanced stability. It is possible to obtain the high working voltage of the supercapacitors by choosing a proper electrode material. Both increase of the working voltage and high energy density of the metal oxide electrode result in a significant increase of the overall energy density of the supercapacitors.
Hence, the RuO$_2$ loaded TiO$_2$ electrode employed as working electrode in the supercapacitors.

5.C.1 Supercapacitive performance of RuO$_2$ loaded on TiO$_2$ nanoparticles

5.C.1.1 Optimization of potential window

The capacitive behavior of RuO$_2$ loaded TiO$_2$ nanoparticles is shown fig. 5.15 (a). The operating potential window for SILAR deposited RuO$_2$ on TiO$_2$ nanoparticle films was found to be 0 to +1000 mV/SCE, which is slightly larger than the reported for the RuO$_2$ thin films in aqueous electrolyte. This results obtained might be due to the increase in electroactive sites and porous structure of the film.

Fig. 5.15 (b) shows charge–discharge (Q-t) plots of RuO$_2$ loaded TiO$_2$ films within 0-1000 mV/SCE potential windows. Charge–discharge curve within potential range 0 to +1000 mV/SCE shows symmetric behavior. The maximum utilization of the material will be obtained in the potential range 0+1000 mV/SCE. Few milicoulomb charges can be stored in 20 second and delivered in same time by the electrode.

![Diagram](image.png)

**Fig. 5.15** (a) Cyclic voltammetric behavior of RuO$_2$ on TiO$_2$ nanoparticles in 0.5M H$_2$SO$_4$ electrolyte at can rate 20mV.s$^{-1}$ within upper potential limit.
Fig. 5.15 (b) Typical charge-discharge (Q-t) curve within 0 to +1000 mV/SCE potential window.

5.C.1.2 Effect of film thickness

Further effect of deposited mass of RuO$_2$ on specific and interfacial capacitance were studied in 0.5M H$_2$SO$_4$ concentration at 20 mV.s$^{-1}$ scan rate. Fig. 5.16 (a) shows the variation of deposited material RuO$_2$ as a function of cyclic voltammogram in 0.5M H$_2$SO$_4$ solution. Fig. 5.16 (b) shows the variation of specific and interfacial capacitances with deposited mass of RuO$_2$ on TiO$_2$ nanoparticles. It reveals that increasing trend of interfacial capacitances values with deposited mass of RuO$_2$ up to its critical value of deposited material. However, specific capacitance shows the peak value at middle; firstly the specific capacitance increases up to 30 F.g$^{-1}$ and again decreases up to the 25 F.g$^{-1}$. Results depicted that the interfacial capacitance increases due to the high surface area offered by TiO$_2$ nanoparticles. Decrease in the specific capacitance compared with RuO$_2$ electrode, owing to resistance offered by the TiO$_2$ nanoparticles. Specific capacitance shows peak value at 0.450 mg.cm$^{-2}$ deposited weight, may be due to dominancy of the double layer capacitance by TiO$_2$ nanoparticle, at initially. The maximum specific capacitance of 30 F.g$^{-1}$ was obtained for
0.450 mg.cm\(^{-2}\) deposited mass and correspondingly interfacial capacitance 0.35 F.cm\(^{-2}\) was obtained.

![Cyclic voltammograms in 0.5 M H\(_2\)SO\(_4\) electrolyte for different thicknesses of RuO\(_2\) loaded on TiO\(_2\) nanoparticles film electrodes mg.cm\(^{-2}\) at scanning rate 20 mV.s\(^{-1}\).](image)

**Fig. 5.16** (a) Cyclic voltammograms in 0.5 M H\(_2\)SO\(_4\) electrolyte for different thicknesses of RuO\(_2\) loaded on TiO\(_2\) nanoparticles film electrodes mg.cm\(^{-2}\) at scanning rate 20 mV.s\(^{-1}\).

![Variation of interfacial and specific capacitance with thickness of RuO\(_2\) loaded on TiO\(_2\) nanoparticles at 20 mV.s\(^{-1}\) scan rate.](image)

**Fig. 5.16** (b) Variation of interfacial and specific capacitance with thickness of RuO\(_2\) loaded on TiO\(_2\) nanoparticles at 20 mV.s\(^{-1}\) scan rate.
5.C.1.3 Effect of scan rate

The cyclic voltametric (CV) curves at different scan rates are shown in fig. 5.17 (a). It was found that, the area under curves was slowly increased with the scan rate. This shows that the CV currents are directly proportional to the scan rates of CV, which demonstrates an ideal capacitive behavior. Since this proton transfer process is slow, higher scan rate leads to either depletion or saturation of the protons in the electrolyte inside the electrode during the redox process. This mainly results in the increase of ionic resistivity leading to drop in the capacitance of the electrode. Fig. 5.17 (b) shows the variation of specific and interfacial capacitance with scan rate. The decreasing trend of the capacitance suggests that parts of the surface of the electrode material are inaccessible at high charging–discharging rates. Hence, the specific capacitance obtained at the slow scan rates is believed to be closest to that of full utilization of the electrode material. At lowest scan rate 2 mV.s\(^{-1}\), maximum specific capacitance is found to be 90 F.g\(^{-1}\).

![Graph showing CV curves at different scan rates](image)

**Fig. 5.17** (a) The CV curves of RuO\(_2\) loaded on TiO\(_2\) nanoparticles electrode at different scanning rates.
Fig. 5.17 (b) Variation of interfacial and specific capacitance with scan rate.

5.C.1.4 Stability of electrode

The cycle life (stability) of RuO$_2$ loaded TiO$_2$ nanoparticle electrode in 0.5 M H$_2$SO$_4$ was tested by CV. Fig. 5.18 shows the CV curves for 1$^{st}$ and 500$^{th}$ number cycle. The current under curve is decreased by 1.2% up to 500 cycles. We found that our system can withstand about 500 cycles without a significant decrease in the capacity compared with RuO$_2$ electrode, illustrating the stable nature of RuO$_2$ loaded TiO$_2$ nanoparticle electrode in energy storage application.

Fig. 5.18 The CV curves of RuO$_2$ loaded on TiO$_2$ nanoparticles electrode at 1$^{st}$ and 500$^{th}$ cycles. The scanning rate and concentration of H$_2$SO$_4$ were 20 mV.s$^{-1}$ and 0.5 M, respectively.
5.C.1.5 Electrochemical impedance analysis (EIS studies)

In order to investigate the electrochemical characteristics of the supercapacitor electrode/electrolyte interface in a quantitative manner, ac impedance spectroscopic measurements were performed. Fig. 5.19 (a) shows the respective Nyquist plots of supercapacitor cell assemblies based on the high surface area films RuO$_2$ loaded on TiO$_2$ films in the 0.5M H$_2$SO$_4$ aqueous solution. It can be seen from the figure that the cell shows a semicircle in the high frequency region and straight line in the low frequency region. This implies that the supercapacitors have a blocking behavior at high frequencies and capacitive behavior at low frequencies. The impedance plots obtained in this case are similar to that of a transmission line model (TLM), for the porous electrode [30]. The TLM consists of parallel combination of R and C elements interconnected with pore resistance elements, R$_p$. The ESR of the RuO$_2$ loaded TiO$_2$ film, is found to 15 $\Omega$. Phase angle shown in fig. 5.19 (b) close to the 64°, indicating a dominant capacitive behavior. Fig. 5.19 (b) shows a Bode plot; at a phase angles of 55° and 64° about 58% and 44% of the power corresponds to heat production at the internal resistance. Loss factors of electrode 0.49 and 0.62 are calculated at a frequency 0.32 Hz and of 0.4 KHz, respectively in the lower and higher frequency region. The relaxation time constant ($\tau_0$), can be calculated from plots of C’($\omega$) vs. frequency shown in fig. 5.19 (c). Relaxation time ($\tau_0$) is found to 102 ms for the RuO$_2$ loaded on the TiO$_2$ nanoparticles electrode.
Fig. 5.19 (a) Nyquist plot of RuO$_2$ loaded TiO$_2$ nanoparticle electrode in 0.5M H$_2$SO$_4$.

Fig. 5.19 (b) Bode plot of RuO$_2$ loaded TiO$_2$ nanoparticle electrode in 0.5M H$_2$SO$_4$.

Fig. 5.19 (c) A typical plot of real capacitance (C') Vs. frequency (log $f$).
5.C.2 Summary and conclusions

In conclusion, RuO$_2$ loaded TiO$_2$ nanoparticles thin films have been successfully employed as supercapacitor electrode. RuO$_2$ loaded TiO$_2$ nanoparticle electrode shows ideal capacitive behavior within the potential window 0-1000mV/SCE which is slightly higher than the bare RuO$_2$ electrode. Maximum specific capacitance found to be 90 F.g$^{-1}$ at scan rate 2 mV.s$^{-1}$ is smaller than the bare RuO$_2$ electrode. Such decrease in the specific capacitance may be due to the larger ESR value, which is arises due to TiO$_2$ nanoparticles. Smaller relaxation time constant value exhibits a faster energy delivery capability of electrode at a higher power density.

5.D.1 Supercapacitive performance of RuO$_2$ loaded on TiO$_2$ nanoflakes

5.D.1.1 Optimization of potential window

The supercapacitive behavior of RuO$_2$ loaded TiO$_2$ nanoflakes is shown fig. 5.20(a). The operating potential window is found to be 0 to +1000 mV/SCE, which is analogous as RuO$_2$ loaded TiO$_2$ nanoparticle electrode. Fig. 5.20 (b) shows charge –discharge (Q-t) plots of RuO$_2$ loaded TiO$_2$ nanoflake films within 0 to +1000 mV/SCE potential windows. Charge–discharge curve within potential 0 to +1000 mV/SCE shows symmetric behavior. The maximum utilization of the material will be obtained in the potential range 0 to +1000 mV/SCE. Few hundred micro-coulomb charges can be stored in 10 second and same time required to deliver.
Fig. 5.20 (a) voltammetric behavior of RuO$_2$ on TiO$_2$ nanoflakes in 0.5M H$_2$SO$_4$ at 20 mV.s$^{-1}$ within upper potential limit.

Fig. 5.20 (b) Typical charge-discharge (Q-t) curve within 0 to +1000 mV/SCE potential window.

5.D.1.2 Effect of film thickness

The effect of thickness of the RuO$_2$ on TiO$_2$ nanoflakes electrode on the capacitive behavior was studied in 0.5M H$_2$SO$_4$ electrolyte at the scan rate of 20 mVs$^{-1}$. Fig. 5.21 (a) shows CV curves of RuO$_2$.nH$_2$O electrode of different thicknesses which indicate that the current increased with thickness. The variation of interfacial and specific capacitances with thickness is shown in fig. 5.21 (b), it can be seen that the thickness increases
from 0.29 to 0.55 mg.cm\(^{-2}\) the interfacial capacitance was increased from 0.35 to 0.72 mF.cm\(^{-2}\) and specific capacitance was increased 3 to 13 F.g\(^{-1}\).

**Fig. 5.21** (a) Cyclic voltammograms in 0.5 M H\(_2\)SO\(_4\) electrolyte for different weight deposited of RuO\(_2\) loaded on TiO\(_2\) nanoflakes film electrodes mg.cm\(^{-2}\) at scanning rate 20 mV.s\(^{-1}\).

**Fig. 5.21** (b) Variation of interfacial and specific capacitance with thickness of RuO\(_2\) loaded on TiO\(_2\) nanoflakes at scan rate 20 mV.s\(^{-1}\).
5.D.1.3 Effect of scan rate

The high-power property of an RuO₂ loaded TiO₂ electrode can be characterized by varying the scan rate of CV and typical results measured at 100, 50, 20, 10, 5 and 2 mV/s in 0.5M H₂SO₄ are shown in fig. 5.22 (a). Note that all curves in fig. 5.22 (a) show the typical capacitive-like responses, indicating the good high-power performance of this RuO₂ loaded TiO₂ nanoflake electrode. Voltammetric currents are approximately proportional to the scan rate of CV. Based on these CV curves, the total specific capacitance of the electrode can be estimated. At lowest scan rate 2 mV.s⁻¹, maximum specific capacitance is found to be 19 F.g⁻¹.

![Fig. 5.22](a) The CV curves of RuO₂ loaded on TiO₂ nanoflakes electrode at different scanning rates.
Fig. 5.22 (a) Variation of interfacial and specific capacitance with scan rate.

5.D.1.4 Stability of electrode

The cycle life (stability) of RuO$_2$ loaded TiO$_2$ nanoflake electrode in 0.5 M H$_2$SO$_4$ was tested by CV. Fig. 5.22 shows the CV curves for 1$^{st}$ and 500$^{th}$ number cycle. The current under curve is decreased to 0.98% after 500 cycles. We found that our system can withstand about 500 cycles without a significant decrease in the capacity, illustrating the stable nature of RuO$_2$ loaded on TiO$_2$ nanoflake electrode in energy storage application. The RuO$_2$ loaded TiO$_2$ nanoflake electrode is more stable compared with the RuO$_2$·nH$_2$O, RuO$_2$ loaded TiO$_2$ nanoparticle electrode.
Fig. 5.22 The CV curves of RuO$_2$ loaded on TiO$_2$ nanoflakes electrode at a) 1$^{st}$ and b) 500$^{th}$ cycles. The scanning rate and concentration of H$_2$SO$_4$ were 20 mV/s and 0.5 M, respectively.

5.D.1.5 Electrochemical impedance analysis (EIS studies)

Fig 5.23 (a) shows Nyquest plot of RuO$_2$ loaded TiO$_2$ nanoflakes electrode that a very small kinetic arc at high frequency implying charge transfer controlled regime and straight line at low frequencies indicating the capacitive regime. This result implies material is suitable for fabrication of low leakage capacitors. In general, a supercapacitor behaves as a pure resistor at high frequencies and as capacitor at low frequencies. In the mid frequency range, it behaves as a combination of resistor and capacitor, while the electrode porosity and thickness of electroactive materials play vital role in the determination of capacitance values. This is in conformity with the transmission line model (TLM). The above mentioned effect shifts the low frequency capacitive behavior towards more resistive values along the real axis, from which the equivalent distributed resistance (EDR) arising due to the uneven porous nature of the electrode material can be calculated. From the high frequency intercept of the semicircle, the equivalent series
resistance (ESR) can determine. In the present case, the ESR value is higher (- 20 Ω) due to additional EDR arising from the resistance offered by the diffusion of ions through the pores, which contributes to the overall resistance value. Fig. 5.23 (b) shows a Bode plot; at a phase angles of 38° and 70° about 79% and 34% of the power corresponds to heat production at the internal resistance. A loss factors of electrode 0.36 and 1.27 are calculated, respectively in the lower and higher frequency region. The relaxation time constant ($\tau_0$), can be calculated from plots of $C'(\omega)$ verses frequency shown in fig. 5.23 (c). Relaxation time ($\tau_0$) is found to 82 ms for the RuO$_2$ loaded on the TiO$_2$ nanoflakes.

![Nyquist plot](image)

**Fig. 5.23** (a) Nyquist plot of RuO$_2$ loaded TiO$_2$ nanoflakes electrode in 0.5M H$_2$SO$_4$.

![Bode plot](image)

**Fig. 5.23** (b) Bode plot of RuO$_2$ loaded TiO$_2$ nanoflakes electrode in 0.5M H$_2$SO$_4$. 
5.D.2 Summary and conclusions

In conclusion, RuO$_2$ loaded TiO$_2$ nanoflakes thin films have been successfully employed as supercapacitor electrode. Maximum specific capacitance found to be 19 F.g$^{-1}$ at 2 mV.s$^{-1}$ scan rate, which is smaller than the RuO$_2$.nH$_2$O and RuO$_2$.nH$_2$O loaded on TiO$_2$ nanoparticles electrodes. Such decrease in the specific capacitance may be due to the larger ESR value, which is arises due to TiO$_2$ nanoflakes/substrate or electrode/electrolyte interface. Smaller relaxation time constant value compared to the RuO$_2$ loaded on TiO$_2$ nanoparticle exhibits a faster energy delivery capability of electrode at a higher power density. This demonstrates RuO$_2$ loaded on TiO$_2$ nanoflake electrode has the potential application in short duration pulse devices.

Fig. 5.23 (c) A plot of real capacitance (C’) Vs frequency (log f).
References