CHAPTER 4

Ti/TiO₂ ELECTRODE PREPARED BY THE THERMAL DECOMPOSITION OF TiCl₃ AND HNO₃

4.1 Introduction

TiO₂ has been one of the most extensively studied oxides because of its remarkable optical and electronic properties. TiO₂ film in anatase phase could accomplish the electrocatalytic reduction of organic compounds. It has many applications in the field of electro-organic synthesis. From the point of view of practical use, the fixation of TiO₂ onto a substrate is very important and some methods to fix the TiO₂ particles have been developed. Consequently, a low-cost preparation and fixation of the TiO₂ electrocatalyst with nanosized particle is necessary for practical applications. Many deposition methods such as thermal and anodic oxidation of titanium, electron beam evaporation, chemical vapor deposition, plasma enhanced chemical vapor deposition, reactive sputtering, sol-gel, spray pyrolysis etc have been reported to prepare nanometer-sized particle powder or thin films [1].

In this method TiCl₃ solution were prepared in different concentrations 0.05, 0.10, 0.15 and 0.20 N using TiCl₃, HNO₃ (5.0%v/v) and isopropyl alcohol (Merck). In this preparation the concentration of HNO₃ and isopropyl alcohol were kept constant and TiO₂ films have been deposited on titanium substrate by slow hydrolysis of TiCl₃ solution. Reaction of Ti (III) with O₂ is rate determining step in TiO₂ formation. The TiOH²⁺ is the only reactive species as per the reactions;

\[ \text{Ti}^{3+} + \text{H}_2\text{O} \rightarrow \text{TiOH}^{2+} + \text{H}^+ \] (1) and

\[ \text{TiOH}^{2+} + \text{O}_2 \rightarrow \text{TiO}_2 + 2\text{OH}^- \] (2)
The reaction (1) should have rapid pre equilibrium. It was found that; rate of hydrolysis was increased resulting into TiO₂ precipitate formation in bulk of solution without film formation on the substrates. So the solution was prepared at low temperature by adding HNO₃ slowly and isopropyl alcohol with the above given concentrations of TiCl₃, at 10°C and maintained at 10°C for 20 minutes and then allowed to raise to room temperature. A stable clear yellow solution is obtained.

These solutions were sprayed over pretreated substrate titanium strips. And film was dried in an oven at 100-110°C. The metal strip was placed in a muffle furnace for 25 minutes. This procedure was repeated at least six times to get a good coating of TiO₂ on titanium metal. Ti/TiO₂ electrodes were coated by the above procedure at 500°C and 600°C. The electrode prepared by the above procedure remained electrochemically active.

The prepared electrodes were subjected to surface morphology and phase study of TiO₂ on titanium substrate by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). Based on these studies the electrode prepared at 600°C with the concentration of 0.15N TiCl₃ electrode was chosen for further corrosion studies and cyclic voltammetric studies. For the preparative electrolysis titanium mesh was used to prepare Ti/TiO₂ electrode by the same procedure.

Results and discussion

4.2 Surface morphology studies

Surface morphology of the coated TiO₂ films was studied by Scanning Electron Microscopy (SEM). The SEM micrographs of TiO₂ film prepared from TiCl₃ with HNO₃ by thermal decomposition method at 500°C, 600°C are given in Fig: 4.1. A, B
The SEM micrographs of Ti/TiO$_2$ electrodes prepared at 500$^\circ$C show more visible cracks than the electrodes prepared at 600$^\circ$C. At 500$^\circ$C with 0.05N TiCl$_3$ the formation of TiO$_2$ film on the substrate was less (Fig 4.1.A. a) compared to electrodes prepared at higher concentration (Fig: 4.1.A. b, c, d). These micrographs prepared at 500$^\circ$C show the well-known cracked mud structure, typical of high content conductive metallic oxide structure [2]. As the concentration of the precursor increases TiO$_2$ film formation is also increased as also reported by other workers [3]. In this case, it has been attributed to the high acidity of HNO$_3$ 1:1 (v/v) (pH 1.5) used to dissolve the precursor salts, resulting in partial dissolution of the titanium-support being responsible for the enhanced TiO$_2$ film on the substrate titanium. Presence of more cracks has good stress bearing ability and they have more surface area than even surfaces [4]. At 600$^\circ$C small round particles of TiO$_2$ formed compared to the electrodes prepared at 500$^\circ$C. As the concentration of TiCl$_3$ increased, that led to few cracks on the electrode surface (Fig: 4.1.B. g, h) than compared with the electrode prepared at lower concentration of TiCl$_3$ (Fig: 4.1.B. e, f).

It is also observed that the surface morphologies and roughness of the TiO$_2$ films are different at different calcination temperatures. The surface morphology and roughness of the thin film occur to change significantly at these two different temperatures. At 500$^\circ$C the anatase particles grow and connect together on the surface and the film shift into the agglomerated state. The growing processes of anatase crystals in solutions and calcination conditions are different. According to the principle of lowest energy growth [5], the crystals can keep stable by regulating their morphologies and grow into round particles through diffusion to maintain their lowest surface area free-energy under heating conditions and the crystals can adjust their morphologies into round figures to achieve the lowest surface free energy which actually happened in the electrodes prepared at 600$^\circ$C.
Fig: 4.1. A SEM Micrographs of TiO$_2$ film on titanium prepared at 500$^\circ$C from

(a) 0.05N, (b) 0.10N, (c) 0.15N, (d) 0.20N of TiCl$_3$ with HNO$_3$ (5.0% v/v)
Fig: 4.1.B SEM Micrographs of TiO$_2$ film on titanium prepared at 600$^\circ$C from

(e) 0.05N, (f) 0.10N, (g) 0.15N, (h) 0.20N of TiCl$_3$ with HNO$_3$ (5.0%v/v)
Therefore the anatase crystals with large length-diameter ratio may decrease in length and gradually become approximate round figures with smaller diameters under heating conditions, the changing process was achieved by the diffusion and transformation of TiO₂ crystals. At the same time, the residual TiCl₃ molecules decomposed and crystallized into anatase phase on the surface of the existing anatase crystals under heating conditions and the length of the anatase crystals decreased and regulated into approximate round figures through diffusion to obtain the lowest surface free energy, the volume of crystals became larger for the growth of the crystals.

At 600°C the SEM micrographs show the TiO₂ film consists of spherical particles. Moreover, it can be seen that some particles getting agglomerated probably due to a severe thermal treatment. Kolan’ Ko et al reported the nano crystalline TiO₂ with particle size 0-24nm were obtained using hydrothermal treatment of TiOSO₄ solution at 523K for 6 hour. In the case of hydrothermal treatment of 0.28M TiO(C₂O₂)₂ aqueous solution, Kolen’ Ko et al reported that the rate of nucleation and recrystallization are comparable and therefore leads to the formation of mesoporous TiO₂ with 60-100nm [6]. Daniele et al have reported [7] that TiO₂ nanoparticles with a mesoporous structure can be prepared in one step and at low temperature (273K) using ammonium bromide as catalysts. Bromide can enhance the crystallization of anantase phase accelerating the nucleation step than the growth leading to very small nanocrystalline particles of the film. One of the advantages of Daniele’s procedure was that highly crystalline TiO₂ films can be deposited on fragile organic substrates such as cellulose fibers, since no calcination is required to obtain the anatase phase. In addition, smaller TiO₂ crystal were reported by Sanhez et al [8-10] by the hydrolysis of titanium metal alkoxides in the presence of
complexing agent ligand, such as acetyl acetone and a non-complexing organic acid such as p-toluene sulfonic acid, followed by ageing at 333-353k, leads to non-aggregated sols of nanocrystalline particles which size can be found between 2-4nm. The film thickness and film quality of the thin films prepared on the substrate are uniform and homogeneous.

4.3 Microstructure analysis of Ti/TiO₂ by X-Ray diffraction

Fig: 4.2. A, B show the XRD pattern of the electrodes prepared by the thermal decomposition method with various concentration of TiCl₃ with HNO₃ as oxidizing agent at two different temperatures. XRD pattern of all the electrodes prepared show the film TiO₂ formed on the substrate titanium with the peak corresponding to 2θ values of anatase phase. The microstructures of the electrodes explain the effect of temperature, the concentration of TiCl₃, pH and the nature of the oxidizing agent.

Generally, it was known that the intensity and full width and half minimum (FWHM) of XRD are related with crystallinity and the crystalline size. The XRD peak intensities are weak and broad when the sample is in amorphous state or in low crystalline in nature, and / or a particle size is very small [11]. XRD pattern of Ti/TiO₂ prepared with different concentrations of TiCl₃ at 500 and 600°C show anatase phase with (110) peak.

The high intensity of the XRD peaks of the thin film increases with calcination temperature and with increase of TiO₂ content due to the improvement in crystallinity. The amorphous to anatase phase transformation occurred when the concentration of TiO₂ content increased. Average crystal size of anatase grains of the film TiO₂ in Ti/TiO₂
coating is in the range of 14 - 68.78nm calculated by means of the Scherrer equation [12]. Line positions of titanium and anatase crystalline structures are marked as ‘Ti’ and ‘A’ respectively.

The anatase (110) occurred at $2\theta = 52.90$ and 25.82. Any contributions to broadening due to non-uniform stress were neglected, and the instrumental line-width in the XRD apparatus was subtracted. The calculated crystallite size of the thin films is listed in Table: 4.1. It is observed from the results that the TiO$_2$ particle size depends on the calcination temperature and TiO$_2$ content. The calculated crystallite size for the electrodes prepared at 500$^\circ$C is in the range from 27-68nm, but with same concentration of TiCl$_3$ at 600$^\circ$C the range of the crystallite size is between 14-27.9nm. The anatase crystallite size of the film TiO$_2$ decreases as the calcination temperature increase.

It can be seen in the electrodes treated at 600$^\circ$C that, together with an increase in the intensity of the anatase which points to further crystallisation of the amorphous component of the dioxide, there appear low-intensity peak related to anatase. The total rate of a transformation from amorphous to anatase is dependent upon both nucleation and growth rates. And since HNO$_3$ was added which gave high acidic pH, this attributes to the formation of anatase phase in the electrodes prepared both at 500$^\circ$C and 600$^\circ$C [13]. Generally the high temperature calcination at 600$^\circ$C not only changed the structure of the film catalysts and also passivated the film catalysts. Thus HNO$_3$ activated the film catalysts and had comparative strong oxidation effects on the film, which could activate the TiO$_2$ film effectively while disposing the impurities on the film surface. Therefore the addition of HNO$_3$ brought out amorphous to anatase crystalline phase and thus
contributing towards better electrocatalytic activity of the electrode Ti/TiO₂. Besides the characteristic diffraction peaks corresponding to the titanium substrate also appeared in the patterns because the film was thin and porous [14].

At 600°C the characteristic peak corresponding to anatase (2θ = 25.6) was formed as the high intensity peak which confirms the TiO₂ predominantly formed as anatase may be due to the high acidic pH by the addition of the oxidizing reagent HNO₃ added to prepare the solution with TiCl₃ for the film deposition on the titanium substrate. The results obtained from the XRD spectrum, the crystal growth and the phase transformation from amorphous to mainly anatase phase in the film is controlled by the calcination temperature, concentration of the precursor and pH of the solution. The various phases of the specimen were identified by matching each characteristics of XRD peak with those in JCPDS files. The primary particle size of TiO₂ film is calculated using Scherrer equation from XRD peak position and full width half maximum (FWHM). The crystallite size of the thin films determined from broadening of corresponding XRD peaks by Scherer equation [15] is

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

D is crystallite size of the composite thin films
λ is wavelength of X-Ray (Cu Kα = 1.5406Å) radiation
K is taken as 0.94
β is the angle with at half maximum height
θ is the half diffraction angle of the centroid in degree.
Fig: 4.2. A X-Ray diffractograms of Ti/TiO₂ electrode prepared at 500°C from (a) 0.05N, (b) 0.10N, (c) 0.15N, (d) 0.20N of TiCl₃ with HNO₃ (5.0%v/v)

Fig: 4.2. B X-Ray diffractograms Ti/TiO₂ electrode prepared at 600°C from (a) 0.05N, (b) 0.10N, (c) 0.15N, (d) 0.20N of TiCl₃ with HNO₃ (5.0%v/v)
XRD pattern of the electrodes demonstrated that the TiO$_2$ nano particles were of homogeneous anatase structure with low crystalline and average size calculated from Scherrer equation are given in the Table: 4.1

**Table: 4.1 Size of the crystal grain of anatase and rutile TiO$_2$ in the film catalysts**

<table>
<thead>
<tr>
<th>Preparation conditions</th>
<th>Anatase</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>θ ($^\circ$)</td>
</tr>
<tr>
<td>Concentration of TiCl$_3$</td>
<td>Calcination Temperature</td>
</tr>
<tr>
<td>0.05N</td>
<td>500$^\circ$C</td>
</tr>
<tr>
<td>0.10N</td>
<td>500$^\circ$C</td>
</tr>
<tr>
<td>0.15N</td>
<td>500$^\circ$C</td>
</tr>
<tr>
<td>0.20N</td>
<td>500$^\circ$C</td>
</tr>
<tr>
<td>0.05N</td>
<td>600$^\circ$C</td>
</tr>
<tr>
<td>0.10N</td>
<td>600$^\circ$C</td>
</tr>
<tr>
<td>0.15N</td>
<td>600$^\circ$C</td>
</tr>
<tr>
<td>0.20N</td>
<td>600$^\circ$C</td>
</tr>
</tbody>
</table>

**4.4 Corrosion studies**

**4.4.1 Tafel polarization technique**

The Tafel polarization curves obtained for the electrode Ti/TiO$_2$ and titanium substrate are given in Fig: 4.3 and 4.4 and also the passivation graphs for the same are given in Fig: 4.5 and 4.6. The various parameters calculated from Tafel technique are given in Table: 4.2.

Changing the kinetics of cathodic and anodic reactions will lead to different open circuit potentials. TiO$_2$ coating changes the slope of anodic and cathodic branches of
Tafel curve and as its results the kinetic of cathodic and anodic reaction will change, so open circuit potential of coated sample will shift to positive direction.

In the coated sample, the cathodic polarization will occur immediately when TiO₂ particles are exposed in 0.1M H₂SO₄. As the anodic reaction will change the corrosion rate \( i_{\text{corr}} \) will decrease due to applied TiO₂ coating on titanium.

In the case of coated sample the anodic reaction is related to TiO₂ particle and it is related to titanium in the uncoated one. TiO₂ particles increase the contact between coating and H₂SO₄ solution, so the intensity of anodic reaction will increase. As the TiO₂ nano particles increases the homogeneity and uniformity of coating and also decrease the defects of coating. From the XRD analysis the particle size formed are of nano scale (Table: 4.1) therefore the nanoparticles control defects on molecular level and will lead to increase corrosion protection properties.

From the Table 4.2 the corrosion parameters value confirms the findings that the coated titanium substrate has excellent corrosion resistance compared with uncoated and also corrosion rate calculated from polarization (C.R = 0.00019mm/year) for Ti/TiO₂ shows more corrosion resistance than the uncoated titanium (C.R=1.3mm/year). Corrosion rate (mmpy), Ecorr (mv vs SCE), passivation range Ep (mA) and passivation current Ip (A) are reported in Table 4.2 and illustrated in Fig: 4.3 and 4.4.

From the Table: 4.2, it is shown that the calculated parameters, for the electrode Ti/TiO₂ show that the film TiO₂ gives prefect passivity when compared to the uncoated substrate titanium.
Table: 4.2 Results obtained from Tafel polarization techniques

<table>
<thead>
<tr>
<th>System studied</th>
<th>Passivation Range (mV)</th>
<th>$E_{corr}$ (mV vs SCE)</th>
<th>$I_p$ (A)</th>
<th>CR (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/TiO$_2$</td>
<td>(-0.5632) to (+2.338)</td>
<td>-0.047</td>
<td>-2.3338</td>
<td>19.06x10$^{-6}$</td>
</tr>
<tr>
<td>Titanium</td>
<td>(0.0955) to (+0.9943)</td>
<td>-0.556</td>
<td>-2.8173</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Fig: 4.3 Tafel polarization plot of Ti/TiO$_2$ electrode in 0.1M H$_2$SO$_4$ prepared from 0.15N of TiCl$_3$ with HNO$_3$ (5.0%v/v) at 600°C
Fig: 4.4 Tafel polarization plot of titanium substrate in 0.1M H$_2$SO$_4$

Fig: 4.5 Passivation plot of Ti/TiO$_2$ electrode in 0.1M H$_2$SO$_4$ prepared from 0.15N of TiCl$_3$ with HNO$_3$ (5.0%v/v) at 600°C
4.4.2 Electrochemical impedance spectroscopic studies

Fig 4.7 and 4.8, show impedance curves for Ti/TiO₂ and the titanium substrate. The electrochemical parameters measured from these curves are given in Table 4.3. From the obtained data, the anodic current density (\(i_{corr}\)), it is evident that coated titanium has good tendency of corrosion resistance behavior. By applying TiO₂ particle on titanium the corrosion resistance in 0.1 M H₂SO₄ has shown remarkable improvement due to the stable and inactive TiO₂ coating. And these findings again are confirmed by the \(E_{corr}\) value obtained from Fig: 4.5, 4.6, which show the relationship between corrosion potential \(E_{corr}\) (mv vs SCE) for the coated and uncoated sample. This indicates the open circuit potential (OCP) of TiO₂ particle is nobler than the bare titanium metal.

The calculated parameters from Tafel polarization techniques like passivation range (\(E_p\)) corrosion potential \(E_{corr}\) (mv vs SCE), passivation current \(I_p\) (A) and corrosion resistance \(CR\) (mmpy) are in good agreement with the parameters calculated from
AC-impedance spectroscopic techniques like phase angle ($\theta$), charge transfer resistance $R_{ct}$ ($\Omega$), film resistance $R_F$ ($\Omega$) and corrosion current $I_{corr}$ (mA/cm$^2$) for both coated titanium and uncoated titanium substrate in 0.1M H$_2$SO$_4$.

Fig: 4.7 Impedance spectroscopic plot of Ti/TiO$_2$ electrode in 0.1M H$_2$SO$_4$ prepared from 0.15N of TiCl$_3$ with HNO$_3$ (5.0%v/v) at 600°C

Fig: 4.8 Impedance spectroscopic plot of titanium substrate in 0.1M H$_2$SO$_4$
Table: 4.3 Results obtained from electrochemical impedance spectroscopic techniques

<table>
<thead>
<tr>
<th>System Studied</th>
<th>Phase Angle ($\theta$)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_F$ (Ω)</th>
<th>$I_{corr}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/TiO₂</td>
<td>48°</td>
<td>400</td>
<td>100</td>
<td>0.04047</td>
</tr>
<tr>
<td>Titanium</td>
<td>25°</td>
<td>1.1</td>
<td>-</td>
<td>11.85</td>
</tr>
</tbody>
</table>

The charge transfer resistance ($R_{ct}$) and $I_{corr}$ (mA/cm²) calculated from the AC-impedance technique for the electrode Ti/TiO₂ and the uncoated titanium substrate are reported in Table 4.3. From the Table: 4.3, it is found that the phase angle value for the coated electrode is 48 and the range of values for phase angle from 40 to 70 indicates [16, 17] that the impedance has a significant contribution in the corrosion resistance properties of the electrode TiO₂ for which the measured phase angle value is 48 compared to the uncoated titanium substrate for which the phase angle value is 14. A decrease of the maximum absolute value of phase angle of the electrode is attributed to the decrease of the corrosion resistance of the metal [18-21].

4.5 Cyclic voltammetric analysis of Ti/TiO₂ in H₂SO₄

Cyclic voltammograms were recorded for Ti/TiO₂ electrode prepared from a solution of TiCl₃ and HNO₃ (0.15N TiCl₃ at 600°C) and presented in Fig: 4.9. The electrolyte was 1.0 M H₂SO₄. The cyclic voltammogram has a reduction peak of Ti⁴⁺ to Ti³⁺, coupled with H₂ evolution. The peak potential is around -560mv/SCE. At -480mv/SCE a well defined peak was observed in the reverse. This peak is due to the surface oxidation of Ti³⁺ formed to Ti⁴⁺ at the electrode surface. Thus this redox cycle is consistently maintained throughout the process.
From this cyclic voltammogram the redox electrocatalytic activity of Ti/TiO$_2$ electrode was well established. The difference in the cathodic and anodic peaks potential showed the process is a quasi reversible process.

Fig: 4.9 Cyclic voltammogram of Ti/TiO$_2$ electrode in 1.0 M H$_2$SO$_4$ prepared from 0.15N of TiCl$_3$ with HNO$_3$ (5.0%v/v) at 600°C

4.5.1 Cyclic voltammetric analysis of Ti/TiO$_2$ in H$_2$SO$_4$ with fumaric acid

Organic compounds are found to be adsorbed on electrode surfaces when their electrochemical behaviors are investigated in aqueous solutions. These adsorbed species give rise to the so called adsorption currents. Such adsorbed monolayer redox species can catalyze a number of other electrochemical reactions.

As a group monolayer redox processes are one of the simplest ones to treat at the phenomenological level, these processes are well described by charge transfer, adsorption effects, and chemical reactions. Since the total charge transfer involved is rather small at the monolayer level, mass transfer effects need not be considered at all.
The monolayer formation process may be represented as

\[ M - O_x + n \text{e}^- \rightleftharpoons M - R \]

The surface redox process to be treated here is quite similar in form. However, both the oxidized and the reduced species are now attached to the electrode surface.

\[ M - O_x + n \text{e}^- \rightleftharpoons M - R \]

Fig: 4.10 A-C presents the cyclic voltammograms of Ti/TiO\(_2\) prepared from 0.15N of TiCl\(_3\) at 600°C obtained with various concentrations of fumaric acid. As discussed earlier when the organic species comes near to the cathode surface it is readily reduced by the presence of Ti\(^{3+}\), a strong reducing agent, present in the electrode surface. As the Ti\(^{3+}\) reduces the organic species, it oxidizes itself to Ti\(^{4+}\) on the electrode surface. Hence there should not be any anodic peak or peak with reduced current should be there in the reverse sweep. Fig: 4.10.A clearly shows this behavior. In the forward sweep peak current also increases due to the reduction of organic species as well as there is no peak in the reverse sweep, which clearly explains the surface redox process as well as fumaric acid reduction in the forward sweep.

On increasing the concentration of fumaric acid the anodic peak is also started to appear. At higher concentration of furmaric acid a well defined anodic peak was observed. (Fig: 4.10.C). This may be due to the crowding of the organic species at the electrode surface, which hinders the surface redox process. Result of this the Ti\(^{3+}\) species on the electrode surface is not involved in the reduction process. The residual Ti\(^{3+}\) present on the electrode surface gets oxidized in the reverse anodic sweep.
Fig: 4.10. A Cyclic voltammogram of Ti/TiO₂ electrode in 1.0 M H₂SO₄ with 0.1mM fumaric acid prepared from 0.15N of TiCl₃ with HNO₃ (5.0%v/v) at 600°C

Fig: 4.10. B Cyclic voltammogram of Ti/TiO₂ electrode in 1.0 M H₂SO₄ with 0.2mM fumaric acid prepared from 0.15N of TiCl₃ with HNO₃ (5.0%v/v) at 600°C
The reduction of fumaric acid to succinic acid at the Ti/TiO₂ electrode is given as follows.

$$2\text{Ti(OH)}_3 + \frac{\text{CHCOOH}}{\text{CHCOOH}} \rightarrow 2\text{TiO}_2 + \frac{\text{CH}_2\text{COOH}}{\text{CH}_2\text{COOH}} + \text{H}_2\text{O}$$

4.6 Preparative electrolysis

A number of preparative scale experiments were carried out under galvanostatic scale experimental conditions to optimize the conditions for preparative electrolysis and to achieve high yield efficiency in the preparation of succinic acid from fumaric acid. Some of these results are summarised in Table: 4.4. The current density was varied from 1.0 - 4.0A/dm² and varied temperature. At lower current densities particularly at 3.0A/dm² fumaric acid reduced to succinic acid with high efficiency.
Table: 4.4 Galvanostatic reduction of fumaric acid at Ti/TiO\textsubscript{2} electrode

Conditions: Amount of fumaric acid taken: 10g

| Electrolyte | 1M H\textsubscript{2}SO\textsubscript{4} |
| Anode | Stainless steel |

<table>
<thead>
<tr>
<th>Expt. No</th>
<th>Current Density (A/dm\textsuperscript{2})</th>
<th>Temperature (°C)</th>
<th>Weight of Succinic Acid (g)</th>
<th>Yield Efficiency (%)</th>
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<tr>
<td>1</td>
<td>1</td>
<td>55</td>
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<td>44.3</td>
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<td>2</td>
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<td>72.4</td>
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<td>8.68</td>
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<td>5</td>
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<td>55</td>
<td>8.70</td>
<td>87.0</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>45</td>
<td>3.80</td>
<td>38.0</td>
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<td>7</td>
<td>3</td>
<td>55</td>
<td>8.70</td>
<td>87.0</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>65</td>
<td>9.30</td>
<td>93.0</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>75</td>
<td>8.65</td>
<td>86.5</td>
</tr>
</tbody>
</table>

The temperature of the electrolysis was varied from 55-65°C as it is given in the experiments at 65°C the yield is very good. And by increasing the electrolyte temperature beyond 65°C causes some destruction to the electrode by means of dissolving the TiO\textsubscript{2} coating. The optimum temperature to get better yield of succinic acid from fumaric acid was taken as 65°C. A high yield (93%) of succinic acid was obtained for the galvanostatic reduction of fumaric acid at Ti/TiO\textsubscript{2} cathode. The yield of succinic acid in all the cases was found to decrease as the temperature increased from 65 to 75°C, which
may be accounted for by competing hydrogen evolution reaction. However, the use of H₂SO₄ medium in the anode compartment is desirable as the cell voltage remains low. In this case, the flow of counter ions (H⁺) from the anode compartment to the cathode compartment is responsible for the cell current.

From the results it was found that the optimum conditions for the reduction of fumaric acid to succinic acid with high yield (93.0%) are the current density at 3.0A/dm² and temperature at 65°C. At lower temperature the yield is low that may be due to the poor solubility of fumaric acid. At higher temperature fumaric acid was totally dissolved i.e. at 65°C that at this temperature the yield is above 90% (Table: 4.4, Expt: 8), by increasing the temperature to 75°C the yield of succinic acid reduced from 93 to 86.5% (Table: 4.4, Expt: 9) that may be due to the TiO₂ film getting corroded to some extent in the electrolyte 1.0 M H₂SO₄.

4.7 Product analysis

The reaction mixture was cooled to room temperature and the unreacted fumaric acid got crystallized out since it is insoluble in aqueous solution, which was filtered out, washed with water and dried. The filtrate was kept in an autoclave at 15°C for 5 hours. The crystals of succinic acid separated, filtered, washed with ice cold water and dried.

The separated crystals were subjected to the ¹H-NMR spectrum of the solid isolated in D₂O. NMR studies showed the result with a single sharp peak at 2.56 d corresponding to the four protons of two methylene groups confirming the formation of succinic acid as the exclusive product from the electro reduction of fumaric acid using Ti/TiO₂.
4.8 Conclusion

From the SEM analysis the Ti/TiO\textsubscript{2} electrodes prepared at 500\textdegree C show the well-known cracked mud structure, typical of high content conductive metallic oxide structure. As the concentration of the precursor increases TiO\textsubscript{2} film formation is also increased. In this case this has been attributed to the high acidity of HNO\textsubscript{3} 1:1 (v/v) of the acid used to dissolve the precursor salts, resulting in partial dissolution of the titanium- support being responsible for the enhanced TiO\textsubscript{2} film on the substrate titanium.

It can also be observed that the surface morphologies of the TiO\textsubscript{2} films are different at different calcination temperatures. The surface morphology and roughness of the thin film occur to change significantly at these two different temperatures. At 500\textdegree C the particles grow and connect together on the surface and the film shift into the agglomerated state. The growing processes of crystals in solutions and calcination conditions are different. At 600\textdegree C small round particles of TiO\textsubscript{2} formed compared to the electrodes prepared at 500\textdegree C. At 600\textdegree C nanocrystalline porous film TiO\textsubscript{2} formed on titanium substrate of particle size in the range of 14-27.9nm and at 500\textdegree C 27-68nm.

The microstructures of the electrodes explain the effect of temperature, the concentration of TiCl\textsubscript{3}, pH and the oxidizing agent. The addition of HNO\textsubscript{3} brought out amorphous to anatase crystalline phase and thus contributing towards better electrocatalytic activity of the electrode Ti/TiO\textsubscript{2}.

From the corrosion studies carried out as the TiO\textsubscript{2} nano particles increases the homogeneity and uniformity of coating and also decrease the defects of coating. Therefore nanoparticles control defects on molecular level and will lead to increased
corrosion protection properties, HNO₃ activated the film catalysts and had comparative strong oxidation effects on the film, which could activate the TiO₂ film effectively while disposing the impurities on the film surface.

From the cyclic voltammetric studies carried out and the results obtained by these studies it clearly revealed that Ti/TiO₂ electrode prepared by thermal decomposition is having a quasi reversible electrocatalytic cycle. Even with this, the electrode can be used to reduce fumaric acid to succinic acid with very high yield which can be comparable with Ti/TiO₂ electrode prepared from titanyl acetyl acetonate.

From the galvanostatic reduction on fumaric acid the high yield obtained by using this electrode is due to the addition of HNO₃ which brought out amorphous to anatase crystalline phase and thus contributing towards better electrocatalytic activity of the Ti/TiO₂ electrode there by yielding the product succinic acid from fumaric acid in high yield.
4.9 References


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