CHAPTER 5
POLARIZATION STUDIES

Polarization study is a very important tool for studying electrochemical reaction as it provides information on current potential relationship for individual anodic and cathodic processes. As reported in Chapter-2 voltametric studies coupled with microstructural observations revealed reduction of TiO\(_2\) in stages through TiO\(_2\) - Ti\(_4\)O\(_7\) - Ti\(_3\)O\(_5\) - Ti\(_2\)O\(_3\) - TiO - Ti[O\(_x\)]. The phases CaTiO\(_3\) and CaTi\(_2\)O\(_4\) have also a role so also the activity of calcium and partial pressure of O\(_2\). This chapter describes and discusses the results of polarization studies carried out for the anodic and cathodic processes in the reduction of TiO\(_2\) as well as oxidation of carbon in molten calcium chloride bath. Here, polarization studies along with prolonged electrolytic experiments at specific cell voltages combined with characterization of the products have been utilized to have an insight of the process.

5.1 Polarization measurements

Figure 5.1 reports the steady-state polarization plots for cathodic reduction of TiO\(_2\) electrode as well as the anodic oxidation of the graphite anode in fused non-pre-electrolyzed CaCl\(_2\) bath at 950°C. The potentials are against the titanium quasi reference (TQR) electrode. The details of the experimental procedure are already reported in Chapter 3. Some values of electrode potentials and current obtained from Figure 5.1 are presented in Table 5.1.

5.1.1 Cathodic process

The rest potential of the TiO\(_2\) cathode is -0.14V against the TQR. This value was reported to be +0.655V for TiO\(_2\) (oxide coated on Ti) by Dring et al. [2005] in molten CaCl\(_2\) bath at 900°C. It was also reported that the value decreases when the working electrode dipped to a greater depth in the electrolyte, and also, at higher temperature. The lower value in the present study might have been due to similar reasons. The four reactions (2.19 to 2.22
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Figure 5.1, Concurrent steady state polarization plots in molten CaCl$_2$ bath at 950$^\circ$C: (a) cathodic for TiO$_2$ and (b) anodic for graphite. Argon flow rate 0.6 lpm. Conditions for TiO$_2$ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30 s, Temperature of heating: 1000$^\circ$C, Duration of heating: 3h.
Table: 5.1 Electrode potentials and cell current at various levels of cell voltages obtained from Figure 5.1

<table>
<thead>
<tr>
<th>Cell voltage, V</th>
<th>Anodic over potential, V</th>
<th>Cathodic over potential, V vs. TQR</th>
<th>Potential due to circuit, V</th>
<th>Cell Current, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>0.981</td>
<td>-2.729</td>
<td>0.190</td>
<td>21.00</td>
</tr>
<tr>
<td>3.5</td>
<td>0.931</td>
<td>-2.379</td>
<td>0.190</td>
<td>17.06</td>
</tr>
<tr>
<td>3.3</td>
<td>0.873</td>
<td>-2.237</td>
<td>0.190</td>
<td>14.39</td>
</tr>
<tr>
<td>3.0</td>
<td>0.796</td>
<td>-2.014</td>
<td>0.190</td>
<td>11.30</td>
</tr>
<tr>
<td>2.8</td>
<td>0.774</td>
<td>-1.836</td>
<td>0.190</td>
<td>9.863</td>
</tr>
<tr>
<td>2.5</td>
<td>0.721</td>
<td>-1.589</td>
<td>0.190</td>
<td>7.762</td>
</tr>
<tr>
<td>2.0</td>
<td>0.722</td>
<td>-1.088</td>
<td>0.190</td>
<td>5.212</td>
</tr>
<tr>
<td>1.5</td>
<td>0.694</td>
<td>-0.616</td>
<td>0.190</td>
<td>3.162</td>
</tr>
<tr>
<td>1.2</td>
<td>0.555</td>
<td>-0.455</td>
<td>0.190</td>
<td>1.945</td>
</tr>
<tr>
<td>1.0</td>
<td>0.436</td>
<td>-0.374</td>
<td>0.190</td>
<td>0.881</td>
</tr>
<tr>
<td>0.8</td>
<td>0.321</td>
<td>-0.281</td>
<td>0.190</td>
<td>0.083</td>
</tr>
<tr>
<td>0.5</td>
<td>0.124</td>
<td>-0.186</td>
<td>0.190</td>
<td>0.005</td>
</tr>
</tbody>
</table>

in Table 2.5), forming calcium titanate, reported by Schwandt and Fray [2005], and the reactions (2.13 and 2.14 in Table 2.4) forming Ti$_3$O$_5$ and Ti$_2$O$_3$, reported by Dring et al. [2005] and Alexander et al. [2006], have the potentials positive to this rest potential.

The plot (a) in Figure 5.1 shows three regions: (i) The first one is in between -0.14 to -0.40V (up to an over-potential of -0.26V) with a slope of -0.045V per decade. This region corresponds to a cell voltage of less than 0.8V and a cell current of less than 0.08A as shown in and Table 5.1. (ii) The second region extends from -0.40V to -0.63V (up to an over-potential of -0.49V) with a slope of -0.375 Volts per decade. The cell voltage and cell current ranges for this region are respectively, 0.8 to 1.5V and 0.08 to 3.16A. (iii) The third region extends from -0.63V onwards with a slope of -2.7 Volts per decade. An extended portion of the later two regions is shown in Figure 5.2. It may be mentioned that Dring et al., [2005] reported formation of TiO at -0.35 to -0.45V (reaction 2.15 in Table 2.4) with respect to TQR electrode at a scan rate of 50 mV/s which moved towards positive direction with decrease in scan rate. The present investigation being at steady state conditions, this may form at potentials lying in region (i) or (ii) mentioned above. Formation of Ti(O)$_x$ from

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TiO (reaction 2.17 in Table 2.4) has been reported to take place at potentials close to -0.97V with respect to TQR which might be occurring in the region (iii) mentioned above. Theoretically, calcium forms at a potential of -1.238V with respect to TQR electrode and Dring et al. [2005] have reported this value to be ~ -1.00V in their experiments. This reaction is likely to occur in the region (iii) and might be reducing TiO₂ / TiO vide reaction 2.6. It may be noted that the slope of -2.7V per decade in region (iii) might be involving diffusion controlled process.

5.1.2 Anodic process

Figure 5.1(b) presents the anodic plot which can be divided into two regions: One (i) starting from the rest potential of 0.05V and proceeding upto 0.40V with a slope of 0.075V per decade and the other (ii) between 0.40 to 0.98V with a slope of 0.400 V per decade. Chen and Fray [2002], in their experiments reported formation of CₓO (adsorbed), CO / CO₂ and Cl₂ (g) at potentials of 1.2, 1.9 and 2.1V versus TQR respectively. However, the anodic potentials reported in Figure 5.1 and Table 5.1 are less than these values.

5.2 Electrolysis and product analysis

From the distribution of electrode potentials between electrodes at various cell voltages as presented in Table 5.1, it is observed that the maximum values of cathodic and anodic potentials corresponding to at 21A are, -2.729 and 0.981V respectively. Dring et al. [2005] and Chen and Fray [2002], who have also used TQR electrodes, reported reduction of Ca²⁺ ion to Ca metal at an overpotential of ~ -1.0V with respect to TQR. Figure 5.1 and Table 5.1 indicate that such a situation prevails at a cell voltage of 2.0V and above. With these information, prolonged electrolysis and product analysis are attempted under some conditions. It may be inferred from the literature studies that broadly two ranges of reduction mechanism exist, i.e. below and above calcium formation potential. The present study aims at a detail understanding of the later case.

5.2.1 Open-circuit condition

Since the cathode rest potential in this study is negative to the standard
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potentials of those reactions forming CaTiO$_3$, Ti$_4$O$_7$, Ti$_3$O$_5$ and Ti$_2$O$_3$ reported in literature [Schwandt and Fray, 2005; Dring et al., 2005], a couple of experiments were conducted at open-circuit conditions. Accordingly, the TiO$_2$ electrode was held in the molten non-pre-electrolyzed CaCl$_2$ bath at 950°C at open-circuit conditions without passage of any current for 15 minutes in the first and, for two hours in the second experiment and then examined through XRD (Figure 5.3). Figure 5.3a shows the pattern for the electrode just before dipping. All the characteristic peaks of TiO$_2$, similar to those presented in Figure 4.3a, are visible. The pattern for the electrode after dipping in molten CaCl$_2$ for 15 minutes does not show any change in phase (Figure 5.3b). However, the XRD pattern for the electrode after dipping for 2hrs shows remarkable change as seen from Figure 5.3c. The main characteristic peaks representing CaTiO$_3$ according to JCPDS file number 22-153 are visible. Besides, most of the TiO$_2$ peaks of Figures 5.3a and 5.3b are also seen but with much lesser intensity counts in comparison to the respective lines of Figures 5.3a and 5.3b, and also to those of the principal line representing CaTiO$_3$ of Figure 5.3c. This suggests that the rutile phase in the TiO$_2$ electrode has not changed by dipping inside non-pre-electrolyzed CaCl$_2$ at 950°C for 15 minutes, whereas the electrode dipped for 2h is transformed to CaTiO$_3$ with a small portion of TiO$_2$ still retained. Its (the later) surface was black, density was 4g/ cm$^3$ and resistivity was still of the order of 10$^6$ ohm.cm. Dring et al. [2005] have reported the possibility of formation of CaTiO$_3$ chemically whereas, Schwandt and Fray [2005] have reported electrochemical formation of this specie from the oxides of Ti such as TiO$_2$, Ti$_4$O$_7$, Ti$_3$O$_5$ and Ti$_2$O$_3$ (reactions 2.19 to 2.22). Since no current has been allowed to pass, the case of electrochemical formation of CaTiO$_3$ does not arise. It might have formed chemically for which sufficient O$^{2-}$ should be available in the bath because no pre-electrolysis has been conducted.

5.2.2 Electrolysis at a cell voltage of 2V

This cell voltage was chosen because the electrolyte was pre-electrolyzed at this cell voltage and it is interesting to note what type of
Figure 5.3 XRD plots for TiO$_2$ pellets: (a) before dipping in molten CaCl$_2$ (b) dipping in molten CaCl$_2$ for 15 minutes, (c) dipping in molten CaCl$_2$ for 2h.

Conditions for TiO$_2$ pellet preparation, Compaction load: 3 ton, Duration of compaction: 30s, Temperature of heating: 1000°C, Duration of heating: 3h. ‘R’ stands for rutile.
reaction products would result in case the TiO$_2$ electrode is placed in the electrolyte during pre-electrolysis stage. Therefore, the TiO$_2$ pellets were electrolyzed at a cell voltage of 2V, one for 15 minutes and the other for 2 hours in molten non-pre-electrolyzed CaCl$_2$ at 950°C. During electrolysis this voltage was consisting of a cathodic overpotential of -1.088 V, an anodic overpotential of 0.722 V and the rest 0.190V due to the electrolyte and circuit resistance (Table 5.1). The electrode after 15 minutes of electrolysis was blackish with a density of 3.82g/cm$^3$ and a resistivity of 2.26 x 10$^6$ ohm.cm. The electrode after two hours of electrolysis was black with a density of 3.12g/cm$^3$ and resistivity of 1.04 x10$^6$ ohm cm. XRD analysis of the two products are shown in Figure 5.4 along with that of the original sample before electrolysis. Unlike the product of 2h dipping of TiO$_2$ electrode in open-circuit conditions as shown in section 5.2.1, no retained TiO$_2$ is observed in this case. The principal peaks of TiO$_2$ are totally absent (Figure 5.4c). Even peaks representing CaTiO$_3$ are also seen in the XRD pattern of the sample electrolyzed for 15 minutes (Figure 5.4b) indicating visible CaTiO$_3$ formation by this time. This implies that the conversion of TiO$_2$ to CaTiO$_3$ is improved under electrolysis at 2V and the process is completed within 2h. However, electrochemical formation of CaTiO$_3$ according to reactions 2.19 to 2.22 is not confirmed in absence of peaks for Ti$_4$O$_7$, Ti$_3$O$_5$, Ti$_2$O$_3$ or TiO which are also the products of these reactions. It may be mentioned that conversion of the entire amount of TiO$_2$ present in the electrode into CaTiO$_3$ has occurred by 2h in this case. However, d-3.38, d-3.02 and d-2.82, the principal peaks for Ti$_4$O$_7$ (JCPDS file no. 18-1402); d-3.54, d-2.19 and d-2.10, the major lines for Ti$_3$O$_5$ (JCPDS file no. 11-217), and d-1.70 and d-2.57, the principal lines for Ti$_2$O$_3$ (JCPDS file number 10-63) are not seen in this pattern. It may therefore, be inferred that formation of CaTiO$_3$ still takes place by the following chemical reaction.

$$\text{TiO}_2 + \text{Ca}^{2+} + \text{O}^{2-} = \text{CaTiO}_3 \quad (5.1)$$

Ca$^{2+}$ and O$^{2-}$ ions are available since the electrolyte is not pre-electrolyzed. Passage of current might be improving mobility of these ions to make this reaction more effective.
Figure 5.4 XRD plots of the TiO$_2$ pellets: (a) before electrolysis, (b) 15 minutes electrolysis, (c) 2h electrolysis. Conditions for TiO$_2$ pellet preparation, Compaction load: 3 ton, Duration of compaction: 30s, Temperature of heating: 1000°C, Duration of heating: 3h.
5.2.3 Electrolysis at a cell voltage of 3V

The TiO₂ pellets were electrolyzed for longer duration at 3V. This cell voltage consists of a cathodic over potential of -2.014 V, an anodic over potential of 0.796 V with 0.190 V due to the cell resistance (Table 5.1). Experiments were carried out for duration of 5, 15, 22 and 37 hours.

5.2.3.1 Current-time characteristics

A typical plot of current versus time obtained during pre-electrolysis with stainless steel rod cathode at 950°C for 2h is shown in Figures 5.5. Figure 5.6 shows the current-time plot for electrolysis of TiO₂ pellet at 950°C for 37h duration along with the plot of Figure 5.5. It is observed from Figure 5.6 (I) that current at the beginning is 7.4A and then decreases to about 1.3A by the end of pre-electrolysis. Then the voltage was increased to 3.0V. The current increased to 9A at the beginning, dropped to 5.4A at 2h, again increased to 8.2A and then fluctuated between 4 to 7A as shown in Figure 5.6 (II). The values obtained for other experiments conducted for 5, 15 and 22 hours (not plotted here) also follow identical patterns. The current-time pattern is not like those obtained by Schwandt and Fray [2005] and Alexander et al., [2006] where the current value falls drastically with time. However, as indicated before, the cathodic overpotential in these series of experiments is -2.014V which is expectedly above Ca²⁺/Ca⁰ potential. This is probably the factor which results in such a current-time plot.

5.2.3.2 Phase analysis of the products

The XRD results are presented in Figures 5.7(b) to 5.7(e) and Table 5.2. Figure 5.7(f) puts all these plots together for a better comparison along with one for pure TiO₂ marked (a) which has also been shown in Figures 5.3 and 5.4. As expected, with increase in electrolysis time, the conversion to titanium is increased. It has been observed that titanium metal formation occurs first at the surface and then continues towards the core. Similar observations have been made by Liu et al. [2005] who have studied the cross section of the partially reduced sample.

The XRD plots make interesting reading. The XRD pattern of the
Figure: 5.5 Current-Time plot for pre-electrolysis at 2V for 2h in molten CaCl$_2$ at 950°C.

Figure: 5.6 Current versus time plot for pre-electrolysis (I) and electrolysis (II) of TiO$_2$ pellet in molten CaCl$_2$ at 950°C.
Cell voltage for pre-electrolysis: 2V, Duration: 2h.
Cell voltage for electrolysis: 3V, Duration: 37h.
Conditions for TiO$_2$ pellet preparation, Compaction load: 3ton, Compaction time: 30s, Temperature of heating: 1000°C, Duration of heating: 3h.
Figure: 5.7 (b) XRD plot of the sample obtained after 5h electrolysis of TiO₂ pellet.
Electrolysis bath: molten CaCl₂ at 950°C, Cell voltage of electrolysis: 3V.
Conditions for TiO₂ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s,
Temperature of heating: 1000°C, Duration of heating: 3h.
Figure: 5.7 (c) XRD plot of the sample obtained after 15h electrolysis of TiO$_2$ pellet.
Electrolysis bath: molten CaCl$_2$ at 950°C, Cell voltage of electrolysis: 3V.
Conditions for TiO$_2$ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s,
Temperature of heating: 1000°C, Duration of heating: 3h.
**Figure 5.7 (d)** XRD plot of the sample obtained after 22h electrolysis of TiO$_2$ pellet.

Electrolysis bath: molten CaCl$_2$ at 950°C, Cell voltage of electrolysis: 3V.

Conditions for TiO$_2$ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s, Temperature of heating: 1000°C, Duration of heating: 3h.
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Figure 5.7(e): XRD plot of the sample obtained after 37h electrolysis of TiO$_2$ pellet.

Electrolysis bath: molten CaCl$_2$ at 950°C, Cell voltage of electrolysis: 3V.

Conditions for TiO$_2$ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s,
Temperature of heating: 1000°C, Duration of heating: 3h.
Figure 5.7(f) XRD plots of the samples obtained after electrolysis of TiO₂ pellets: (a) without electrolysis, (b) 5 h electrolysis, (c) 15 h electrolysis, (d) 22 h electrolysis, (e) 37 h electrolysis. Electrolysis bath: molten CaCl₂ at 950°C, Cell voltage of electrolysis: 3V. Conditions for TiO₂ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s, Temperature of heating: 1000°C, Duration of heating: 3h.
Table: 5.2 Phases obtained after electrolysis of TiO$_2$ pellet for different time durations.
Compaction load: 3 ton, Compaction time: 30 s, Heating temperature: 1000°C, Heating time: 3 h, Bath: molten CaCl$_2$, Temperature of electrolysis: 950°C.

<table>
<thead>
<tr>
<th>Weight of TiO$_2$ pellet before electrolysis, g</th>
<th>Electrolysis duration, h</th>
<th>Weight of the electrolyzed pellet, g</th>
<th>Phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.674 (~4.546 CaTiO$_3$) (~1.604 Ti)</td>
<td>5</td>
<td>3.494</td>
<td>TiO$_2$, CaTiO$_3$, TiO, Ti$_2$O, Ti</td>
</tr>
<tr>
<td>2.60 (~4.42 CaTiO$_3$) (~1.56 Ti)</td>
<td>15</td>
<td>2.663</td>
<td>CaTiO$_3$, Ti$_2$O, TiO, Ti</td>
</tr>
<tr>
<td>3.41 (~5.80 CaTiO$_3$) (~2.05 Ti)</td>
<td>22</td>
<td>2.492</td>
<td>Ti, TiO</td>
</tr>
<tr>
<td>4.23 (~7.19 CaTiO$_3$) (~2.54 Ti)</td>
<td>37</td>
<td>2.527</td>
<td>Ti</td>
</tr>
</tbody>
</table>

Product at 5 h electrolysis shown in Figure 5.7b is basically a mixture of CaTiO$_3$ and TiO$_2$, the intensity counts for the principal lines of each species being 1482 and 461, respectively. This means, though major part of the TiO$_2$ has been converted to CaTiO$_3$, the conversion is not complete even by 5 h, which was achieved during 2 h by electrolyzing at 2 V (Figure 5.4c). Pre-electrolysis of the molten CaCl$_2$ bath is the reason for this difference. Removal of the redox species by pre-electrolysis has slowed down the process in the present case. However, the conversion is by chemical process because the major peaks of Ti$_4$O$_7$, Ti$_3$O$_5$ and Ti$_2$O$_3$, which are the product of electrochemical conversion according to reactions 2.19 to 2.21, are absent. It may also be mentioned that the principal peaks of TiO (d-2.07 and d-1.46: JCPDS file number 9-240), Ti$_2$O (d-2.27: JCPDS file number 11-218) and Ti (d-2.24: JCPDS file number 5-0682) are close to some of the peaks of TiO$_2$ and TiO$_2$. 

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hence these species might have formed in small quantities and still not detected. Figure 5.7c is clearer in this respect since TiO$_2$ has totally vanished by 15h and hence the XRD pattern gives a clear picture of lines representing TiO, Ti$_2$O and Ti metal along with reduced lines of CaTiO$_3$. By 22h only Ti peaks with a small line of TiO stay in picture (Figure 5.7d) and the later one vanishes by 37h (Figure 5.7e). These results indicate that the probable conversion path of TiO$_2$ to Ti metal may be TiO$_2$ - CaTiO$_3$ - TiO - Ti$_2$O - Ti. The final sample obtained after 37h was analyzed and found to contain 1.04% O and had a conductivity of 3.720 X 10$^4$ ohm$^{-1}$.cm$^{-1}$, whereas that of a standard Ti sample was measured to be 1.661 X 10$^3$ ohm$^{-1}$.cm$^{-1}$.

5.2.3.3 SEM Analysis

The SEM micrographs of the titanium metal produced after 37h electrolysis and the standard Ti sample are shown in Figures 5.8 and 5.9 respectively. The WDS graph of the partially reduced sample obtained after 15h electrolysis is shown in Figure 5.10, showing very small Ca peaks in addition to stronger Ti peak, whereas, that corresponding to 37hrs electrolysis shown in Figure 5.11, shows only the peaks of Ti.

5.2.3.4 Probable Reaction Mechanism

These results indicate the probable reaction path to be TiO$_2$ - CaTiO$_3$ - TiO - Ti$_2$O - Ti. Table 5.3 and Figure 5.12 report presence of these species (through the intensity count of the principal peaks of each species) at various durations of electrolysis. The input material TiO$_2$ which has totally vanished by 2h during electrolysis at 2V in non-pre-electrolyzed CaCl$_2$ bath did not vanish by 5hrs in a pre-electrolyzed bath. Ti metal is the only final product by 37h. The intermediate products are CaTiO$_3$, TiO and Ti$_2$O in that order and they appear and vanish. Out of these three species CaTiO$_3$ appears for longer time and relatively at larger amounts (Figure 5.12). Next comes Ti$_2$O. TiO peak height is the least. This indicates that the conversion of CaTiO$_3$ to TiO is slower and that of TiO to Ti$_2$O may be relatively faster. The rate of conversion of Ti$_2$O to Ti may be in between. Conversion of TiO$_2$ to CaTiO$_3$ is probably by chemical route because the principal peaks of Ti$_4$O$_7$, Ti$_3$O$_5$ and Ti$_2$O$_3$, which
Figure: 5.8 SEM micrograph of the titanium metal produced after 37h electrolysis of TiO$_2$ pellet in molten CaCl$_2$. Temperature of electrolysis: 950°C, Cell voltage of electrolysis: 3V. Conditions for TiO$_2$ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s, Heating temperature: 1000°C, Duration of heating: 3h.

Figure: 5.9 SEM micrograph of the standard titanium metal.
Figure: 5.10  WDS graph for partially reduced sample obtained after 15h electrolysis of TiO$_2$ pellet in molten CaCl$_2$. Temperature of electrolysis: 950°C, Cell voltage of electrolysis: 3V.
Conditions for TiO$_2$ pellet preparation: Compaction load: 3 ton, Duration of compaction: 30s, Heating temperature: 1000°C, Duration of heating: 3h.

Figure: 5.11  WDS graph corresponding to Figure 5.8.

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Table 5.3: Intensity counts of the principal peaks of the species during electrolysis

<table>
<thead>
<tr>
<th>Time</th>
<th>TiO₂</th>
<th>CaTiO₃</th>
<th>TiO</th>
<th>Ti₂O</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2621</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>610</td>
<td>1482</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>930</td>
<td>375</td>
<td>620</td>
<td>583</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>0</td>
<td>159</td>
<td>0</td>
<td>1689</td>
</tr>
<tr>
<td>37</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>801</td>
</tr>
</tbody>
</table>

Figure 5.12: Intensity count of the principal peaks at various time durations. (a) TiO₂, (b) CaTiO₃, (c) TiO, (d) Ti₂O, and (e) Ti metal.

are supposed to form along with CaTiO₃ according to reactions 2.19 to 2.21, are not seen in the XRD pattern as indicated in section 5.2.3.2. The next step is the conversion of CaTiO₃ to TiO which may be taking place electrochemically following reaction 2.15. Probably this reaction is slow in comparison to conversion of TiO to Ti₂O and then to Ti metal. As discussed earlier in section 5.2.3.2, the species TiO, Ti₂O and Ti may be already present by 5h, although these are shown as absent in Table 5.3 and Figure 5-12.

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Similarly, Ti$_2$O has also been shown as absent beyond 15h in the said table and figure. However, being a product in between TiO and Ti it might be present in small quantities with Ti and detected in XRD owing to the closeness of most of its peaks to those of Ti metal. Conversion of TiO-Ti$_2$O-Ti might be taking place chemically according to the following reactions:

\begin{align*}
2\text{TiO} + \text{Ca} &= \text{Ti}_2\text{O} + \text{CaO} \\
\text{Ti}_2\text{O} + \text{Ca} &= 2\text{Ti} + \text{CaO}
\end{align*}

Ca might be a product of reaction 2.18. Some TiO might be forming Ti electrochemically following reaction 2.17. The weight of TiO$_2$ electrodes used and the product obtained in these experiments (Table 5.2) confirm to this scheme.

5.3 Inferences

The following inferences may be drawn from the polarization studies presented in this chapter.

(i) The open circuit potentials of the TiO$_2$ cathode and graphite anode are -0.14V and +0.05V, respectively, against TQR electrode. The cathodic open circuit potential is negative to the potentials of reactions forming oxides of titanium and calcium titanate.

(ii) In open circuit conditions dipping the TiO$_2$ in molten non-pre-electrolyzed CaCl$_2$ bath at 950°C for 2 hrs results in conversion of major part of TiO$_2$ to CaTiO$_3$. In an identical bath electrolysis at a cell voltage of 2V makes this process faster so that the entire electrode is converted to CaTiO$_3$ by 2hrs. In a pre-electrolyzed bath this process becomes slower. Yet, this conversion is probably by a chemical process.

(iii) Three regions are observed in the cathodic polarization plot Tafel slopes of (a) -0.045V/ decade below a cell voltage of 0.8V and a current of 0.08A, (b) -0.375V/ decade between the cell voltage of 0.8 to 1.5V and cell current of 0.08 to 3.12A and (c) -2.7V/ decade above this cell voltage. The first two regions may be below calcium formation region, whereas, the third one may be forming calcium.
(iv) The anodic plot shows two active regions. The first one is below a cell voltage of 0.8V with a slope of 0.075V/decade. The second one is beyond this cell voltage with a slope of 0.400V/decade. However, the maximum anodic over-potential obtained at a cell voltage of 3.9V is 0.981V (versus TQR) which is below the potentials of 1.2, 1.9 and 2.1V, reported in literature for formation of CO$_x$, CO/CO$_2$ and Cl$_2$, respectively.

(v) The reaction products after prolonged electrolysis at 3.0V (cathodic over-potential of -2.014V and anodic over-potential of 0.796V) are CaTiO$_3$ in the initial stages followed by TiO, Ti$_2$O and Ti metal, which reaches a stage of Ti(O)$_x$ ($x = 1.04\%$) by 37 hours.

(vi) The proposed reaction scheme involves the following steps:
(a) TiO$_2$ to CaTiO$_3$ by chemical reaction which is fast.
(b) CaTiO$_3$ to TiO by electrochemical route and this step is slow.
(c) TiO might be reducing chemically to Ti$_2$O or Ti directly by Ca formed electrochemically at the cathode. Ti$_2$O formed in the process might also be converted to Ti metal chemically by Ca. Some TiO might be converting directly to Ti electrochemically.