CHAPTER 6

SUMMARY, CONCLUSION AND SCOPE FOR FUTURE WORK

Recent literature survey indicated that AB$_2$ type alloys have high energy density than AB$_5$ type alloys. AB$_5$ alloys have higher rate capabilities. The differences in their electrochemical behavior are due to the different crystal and electronic structures of these two alloys. Literature survey also indicated that it is possible to increase cycle life and other properties of the alloy by changing its composition. Literature survey also indicated that Titanium based alloy metal hydrides are promising candidates for high storage capacity electrode materials. Also, much research has been devoted to the design of TiMn$_2$ based compounds for many practical applications. TiMn$_2$ based alloys offer advantages as hydrogen storage materials.

Literature survey indicated that for the alloy to be used, as a negative electrode in alkaline conditions nickel is an important element as it imparts resistance towards oxidation and is also a good hydrogen recombination catalyst thus helping in the electrochemical properties of the alloy. All the alloys that have been studied have nickel as a primary element and substitutions are carried out by replacing small amount of nickel with other elements like Sn, Al, Co, V, Mn etc. The present investigation uses a different approach of selecting a high capacity nickel free alloy and substitute one of its elements with other elements such as nickel, zirconium or vanadium and study it electrochemical properties in alkaline medium.
The present investigation deals with the following studies using alkaline KOH as the electrolyte.

i) To study the effect of nickel substitution on high storage capacity of TiMn$_2$ alloys.

ii) To study the effect of copper encapsulation on the alloy.

iii) To study the effect of using carbon black (Vulcan XC72) as an additive instead of copper powder.

iv) To study the effect of activation on the electrochemical properties of TiMn$_2$ based alloy.

v) To study the effect of partial substitution of titanium with zirconium.

vi) To study the effect of partial substitution of manganese with vanadium.

The experimental work mainly involved:

i) Preparation of TiMn$_2$ alloys containing nickel

ii) Copper encapsulation of TiMn$_2$ alloy.

iii) Activation of the alloy using HF and H$_2$O$_2$

iv) Preparation of TiMn$_2$ based alloy containing zirconium

v) Fabrication of the alloy electrodes with copper additive.

vi) Fabrication of the alloy electrodes with carbon additive.

vii) Performance evaluation of alloys by electrochemical studies.

The electrochemical studies carried out were

1. Galvanostatic polarization
2. Cyclic voltammetry studies
3. Rate capability studies
4. Cycle life studies
5. Controlled potential discharge studies
6. Linear polarization studies
7. ac impedance studies.

The conclusions that emerged from the present investigation and a brief summary of the findings are given below:

1. Studies on the effect of nickel addition to TiMn$_2$ lead to the conclusion that nickel improves the charge-discharge capacities of the alloy. A maximum capacity of 514 mAh/g was obtained for TiMn$_{1.6}$Ni$_{0.4}$ alloy. The alloys were found to undergo corrosion in alkaline medium. However, the cycling stability also increased with increase of nickel in the alloy. The presence of nickel on the surface of the alloy improved its electrochemical properties. The capacity of the alloy increased with cycle number due to microcracking activation of the alloy. A fully activated alloy is prone to more corrosion and, hence, the capacity decreased thereafter. The efficiency of the alloy also followed a similar pattern. The discharge capability of the alloy was dependent on the discharge current. At low discharge current, charge transfer was the dominant process and at high discharge current, diffusion of hydrogen from the bulk was the rate determining step. The presence of nickel rich layer on the surface of the alloy catalyzed the hydrogen recombination reaction leading to high rate of discharge.

The diffusion coefficients of hydrogen for the alloys as calculated from controlled potential discharge studies revealed that the alloy had low diffusion coefficients. The value was found to increase marginally with the nickel content in the alloy. The diffusion coefficient was also dependent on the state of charge of the alloy. It decreased with decrease in state of charge due to higher affinity for hydrogen on discharge. The ac impedance and dc
polarization techniques were used to find the exchange current density of the alloy, which is a measure of kinetics. The alloy TiMn$_{1.6}$Ni$_{0.4}$ had the maximum exchange current and was found to be dependent on the state of charge of electrode. As the resistance of the electrode increased on discharge, the alloys showed lower exchange current density on discharge. In general, the improvement in electrochemical properties was dependent on the amount of nickel in the alloy and the alloy TiMn$_{1.6}$Ni$_{0.4}$ showed better electrochemical properties than the other alloys.

2. Studies on copper encapsulation of TiMn$_2$ revealed that the corrosion rate of the alloy could be decreased by copper encapsulation. Copper itself does not absorb hydrogen and, hence, does not improve hydrogen absorption properties of the alloy. It acts as a barrier and protects the alloy from corrosion. However, cycling introduces microcracking on the alloy surface and thus the alloy becomes susceptible to corrosion slowly. A copper encapsulated alloy shows better electrochemical properties in terms of higher capacity, high rate discharge capability and cycling. The copper encapsulated alloy also has higher exchange current density indicating its superior properties. However, the diffusion coefficient of hydrogen, which is a bulk property, does not change on encapsulation. Copper coating is only a surface phenomenon.

3. Studies on addition of carbon black (Vulcan XC72) revealed that the corrosion rate of the alloy increased upon use of this additive. Carbon black in the presence of binder forms three dimensional networks leading to a porous structure. This brings about increased contact of the alloy with the alkaline electrolyte leading to extensive corrosion. The discharge capacity, cycling ability and rate capability is much lower than the alloy with copper additive, carbon black also has lower conductivity than copper additives. The exchange current for the carbon added alloy electrode as calculated from dc
polarization and ac impedance studies was also lower than copper added alloy electrode.

4. Activation of the high capacity TiMn_{1.6}Ni_{0.4} alloy was carried out by treatment of the alloy powder with HF and H_{2}O_{2} (Ramya et al 2002). The surface of the alloy gets etched and it makes the oxide layer present on the surface more porous. Etching does not remove the oxide layer. The etched surface is expected to be rich in nickel improving the catalytic properties of the alloy. The presence of higher amount of nickel on the surface has been confirmed by SEM-EDAX analysis.

The activated alloy showed higher capacity than the as produced alloy. A maximum capacity of 614 mAh/g was obtained in lower number of cycles as compared to the as produced alloy. The easier activation of the etched alloy can be attributed to the presence of nickel rich layer on the surface. However, cycle life studies indicate that the activated alloy is more prone to corrosion compared to the as produced alloy. These results suggest that the durability of the as produced alloy is better.

Cyclic voltammetric studies suggest that the alloy can be cycled by cyclic voltammetric technique. Prominent peaks due to charging and discharging can be seen. The area of the peak was dependent on the scan rate. At low scan rate, the charging capacities approached that of galvanostatic method indicating that there is enough time for diffusion process to set in and, hence, the alloy gets charged and discharged fully. A comparison of the capacities of the as produced and etched alloy showed that the capacity of the etched alloy is higher than the as produced alloy. Decrease in capacity (area under the peak) can be seen through comparison of cyclic voltammograms at various cycles indicating corrosion of the alloy.
Comparison of the discharge capacity as a function of discharge current indicates that discharge capacity is lower at high discharge currents. The decrease in capacity is lower for the as produced alloy compared to the etched alloy.

Diffusion coefficients for the activated and the as produced alloy have been calculated by controlled potential discharge experiments. There was marginal decrease in the diffusion coefficient values with decrease in state of charge. Surface modification did not have any effect on the diffusion coefficient of the alloy.

The exchange current density has been calculated using dc polarization and ac impedance methods. The values were higher for the etched alloy compared to the as produced alloy showing better electrochemical characteristics of etched alloy due to its nickel rich surface layer. The exchange current density values decreased with decrease in state of charge. The values obtained using the two methods were comparable.

5. Studies on zirconium substituted alloys $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.6}\text{Ni}_{0.4}$ and $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{Mn}_{1.6}\text{Ni}_{0.4}$ revealed that these alloys are slow to activate and had lower capacity than the non-substituted alloy. The initial capacity, capacity of the first few cycles, was lower than the non-substituted alloy. These could be attributed to the formation of passive oxide layer $\text{ZrO}_2$ on the surface of the alloy. The corrosion properties of this alloy is similar to the other alloys studied where once the maximum capacity is reached, capacity decrease due to oxidation of the alloy in alkaline medium was observed. Rate discharge capability of zirconium substituted alloy was lower than that of the non-substituted alloy. Between the two alloys, studied $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.6}\text{Ni}_{0.4}$ alloy showed higher capacity, higher cycling ability and better rate capability than $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{Mn}_{1.6}\text{Ni}_{0.4}$ alloy.
A study of retention of charge on the two zirconium substituted alloy revealed that Tio.9Zro.iMni.6Nio.4 alloy retained the charge better than the other alloy i.e., self discharge of this alloy was less than the other alloy.

Diffusion of hydrogen in these alloys was found to be similar to the other alloys studied. The exchange current density as calculated from the dc polarization studies was higher for the alloy Tio.9Zro.iMni.6Nio.4. However, the exchange current density values were lower than that of non-zirconium substituted alloy.

6. Vanadium substitution was carried out on a zirconium substituted alloy to study its electrochemical properties. The charge/discharge characteristics, cycling ability and rate capability were lower than the other zirconium substituted alloy. These could be attributed to the extensive corrosion of the alloy, as Vanadium forms oxide layer, which is porous. The diffusion coefficient of hydrogen for the alloy was similar to the other alloys studied. The exchange current density for this alloy was also lower than the other zirconium substituted alloy.

Table 6.1 compares the electrochemical properties of various alloy electrodes studied during the course of this investigation.

6.1 SCOPE FOR FUTURE WORK

All the studies carried out so far reveal that surface characteristics of the alloy and the composition of the alloy are important parameters for the development of metal hydride alloy, which has high capacity and good cycling ability. A proper choice of the alloying element would ensure synergistic effect in catalysis and the design of high capacity alloy. Scope exists for further improvement in metal hydride alloy by identifying alloying element, which
Table 6.1 Comparison of properties for all the alloys studied during the course of this investigation

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Maximum Capacity (mAh/g)</th>
<th>Diffusion coefficient (cm²/s)</th>
<th>Exchange current density (AC impedance) mA/cm²</th>
<th>Exchange current density (Linear Polarization) mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiMn₂</td>
<td>280</td>
<td>1.65 x 10⁻¹¹</td>
<td>34.0</td>
<td>37.9</td>
</tr>
<tr>
<td>TiMn₁₅/₄Ni₀₂</td>
<td>400</td>
<td>1.83 x 10⁻¹¹</td>
<td>43.7</td>
<td>42.9</td>
</tr>
<tr>
<td>TiMn₁₅/₄Ni₀₄</td>
<td>514</td>
<td>2.13 x 10⁻¹¹</td>
<td>55.2</td>
<td>61.2</td>
</tr>
<tr>
<td>TiMn₁₅/₄Ni₁₅</td>
<td>350</td>
<td>2.5 x 10⁻¹¹</td>
<td>39.8</td>
<td>39.0</td>
</tr>
<tr>
<td>Carbon added TiMn₂</td>
<td>180</td>
<td>-</td>
<td>8.74</td>
<td>7.7</td>
</tr>
<tr>
<td>Copper coated TiMn₂</td>
<td>360</td>
<td>-</td>
<td>69.8</td>
<td>58.2</td>
</tr>
<tr>
<td>TiMn₁₅/₄Ni₀₄ (Etched)</td>
<td>615</td>
<td>-</td>
<td>67.1</td>
<td>84.7</td>
</tr>
<tr>
<td>Ti₉₅Zr₀₅Mn₁₅/₄Ni₀₄</td>
<td>454.8</td>
<td>4.3 x 10⁻¹¹</td>
<td>-</td>
<td>21.6</td>
</tr>
<tr>
<td>Ti₉₅Zr₀₅Mn₁₅/₄Ni₀₄</td>
<td>405.8</td>
<td>1.71 x 10⁻¹¹</td>
<td>-</td>
<td>20.0</td>
</tr>
<tr>
<td>Ti₉₅Zr₀₅Mn₁₅/₄V₀₄</td>
<td>186.6</td>
<td>1.85 x 10⁻¹¹</td>
<td>-</td>
<td>18.9</td>
</tr>
</tbody>
</table>
reduces corrosion and enhances hydrogen storage capacity. The composition of the alloy and the percentage of the alloying element are also important. Scope for the future work involves

➢ Study of characteristics of new alloys prepared by varying alloy composition (including alloying elements such as chromium, cobalt, aluminium, tin etc.)

➢ Fabrication of a large sized electrode

➢ Study of electrode characteristics for a large sized electrode.

➢ Fabrication of a battery using a nickel electrode

➢ Study of electrochemical characteristics of the battery

➢ Study of temperature effects on the electrochemical properties of the electrode

➢ Study of effect of temperature on the self discharge characteristics of the alloy electrode