Short communication

Electrochemical synthesis of hexagonal closed pack nickel: A hydrogen storage material

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ABSTRACT

An in situ hydrogen generation and storage technique is demonstrated during the electrodeposition of hexagonal closed pack (HCP) nickel from $NiCl_2$-1-ethyl-3-methylimidazolium chloride ($NiCl_2$-EmimCl) and $NiCl_2 \cdot 6H_2O$-1-ethyl-3-methylimidazolium chloride ($NiCl_2 \cdot 6H_2O$-EmimCl) melts. During electrolysis, the dissolution of hydrogen in nickel takes place due to the electrolysis of water. This results in the production of HCP nickel. The hydrogen content of the electrodeposited nickel from $NiCl_2$-EmimCl was found to be 1.2 wt.%. Thermal analysis showed that the phase transformation from HCP nickel to FCC occurred at 462 °C, releasing hydrogen in the process.

1. Introduction

Hydrogen is an attractive as well as a clean source of energy and therefore is considered to be a future source of energy for transportation. However, the biggest challenge is the development of a material which has fast hydrogenation and dehydrogenation reactions at moderate temperatures.

Extensive research and development activities are ongoing to develop a suitable hydrogen storage material [1–5]. Metal hydrides are promising candidate for hydrogen storage. Magnesium based hydrides stores around 7.6 wt.% of hydrogen [1,4–8]. Complex metal hydrides such as lithium boron hydride ($LiBH_4$) have the capability of storing around 10 wt.% of hydrogen [9,10]. Other boron hydride complexes can store more than 13 wt.% hydrogen [2,3,10]. Yan et al. demonstrated that some metal–organic framework can store about 10 wt.% hydrogen [11]. A recent review paper describes in detail the various strategies which can be used to improve the hydrogen storage in metal–organic framework [12]. Recently, Sebastián et al. [13] showed that the hydrogenation–dehydrogenation process in decalin/napthalene can be accelerated by the addition of platinum catalysts.

One of the methods to produce metal hydrides is by ball milling the material under hydrogen pressure of few atmospheres [2,14]. Another technique for hydride formation involves the cooling of the hydrogen storage material to very low temperatures (<100 K) and then storing the hydrogen [11]. A new hybrid approach of introducing hydrogen into the material was demonstrated by Lu et al. wherein lithium hydroxide was produced from lithium oxide and water. Lithium hydroxide upon reaction with lithium hydride produced lithium oxide and hydrogen [15].

Introduction of hydrogen into the metal to form hydrides require high pressure and more importantly the hydrogen has to be initially produced either from petroleum products or by the electrolysis of water. So these techniques involve multistep and complex processes.

Nickel is a well known metal and is extensively used in nickel metal hydride batteries. The nickel hydrogen phase diagram shows that at high pressures of greater than 100 MPa there is considerable solubility of hydrogen [16,17]. Such high hydrogen fugacity can be achieved by electrochemical deposition. Impure phase of metastable HCP nickel containing 0.1 wt.% hydrogen was produced by electrolysis of nickel sulfate solution [18].

In this communication, we present a new technique to simultaneously produce and store hydrogen. The metastable HCP nickel was synthesized electrochemically from both $NiCl_2$ containing 2 wt.% moisture (determined by thermogravimetric analysis) and $NiCl_2 \cdot 6H_2O$ at 160 °C. After electrolysis, the deposited material was characterized using differential thermal analysis (DTA), X-ray diffraction and scanning electron microscopy techniques. The percentage of hydrogen was evaluated by Midwest Microlab, using a thermogravimetric analysis coupled with gas chromatography technique.

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2. Experimental

Ionic liquid of 1-ethyl-3-methylimidazolium chloride and titanium metal was obtained from Sigma–Aldrich. Typical $NiCl_2$-EmimCl and $NiCl_2 \cdot 6H_2O$-EmimCl molten salt was prepared by mixing 5.4 mole% of nickel salt in EmmiCl in a Pyrex beaker. The experiment was conducted in a Labconco glove box filled with argon. The mixture was stirred continuously for complete dissolution. The end product obtained was a green liquid.

The electrochemical experiments were conducted in a 40 ml Pyrex beaker fitted with a Teflon cap. The Teflon cap had holes for the introduction of electrodes and thermometer. A schematic diagram of the electrolysis setup is shown elsewhere [19]. During the experiment the temperature was monitored continuously. The active area of titanium anode and cathode over which the electrodeposition was performed had a dimension of 25 mm × 15 mm × 0.5 mm. Platinum was used as a quasi reference electrode. The three electrodes were immersed into the electrolyte which was maintained at a constant temperature of 160 °C before a potential of −2.0 V was applied. The electrolysis at constant potential was carried out for 2 h. After the experiment, the electrolyte was stored in a glass bottle. The material deposited at the cathode was thoroughly washed with acetone and water and was analyzed under SEM in JEOL 7000. EDX measurements were also performed to determine the compositions of the electrodeposited material. For XRD analysis, samples were ground and mounted on a silica glass which was then fitted into the Philips PW 3038 diffractometer. The scan rate for the XRD measurement was kept constant at $0.02° \, s^{-1}$ and the sample was scanned from 20° to 90°. DTA analysis was carried out with 5 mg sample in a PerkinElmer DTA 7, with alumina as the reference. A constant heating rate of $10 °C \, min^{-1}$ was maintained and nitrogen gas was passed through the DTA at a rate of $20 \, ml \, min^{-1}$. DTA data was collected using a computer based software program called Pyris provided by PerkinElmer. The hydrogen analysis was performed by Midwest Microlab, using a thermogravimetric analysis coupled with gas chromatography technique.

3. Results and discussion

Fig. 1 compares the diffraction patterns of the electrodeposited nickel from $NiCl_2$ and $NiCl_2 \cdot 6H_2O$ with standard ICDD pattern (ICDD 1-089-7129). It is evident from the XRD that the electrodeposited nickel has HCP structure and no FCC phase is present. However, the broad peak of the diffraction pattern indicates that the deposited Ni is not fully crystalline. Comparing the diffraction
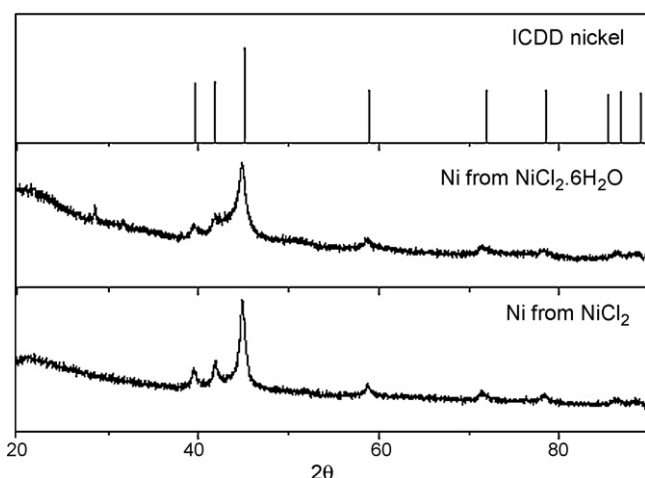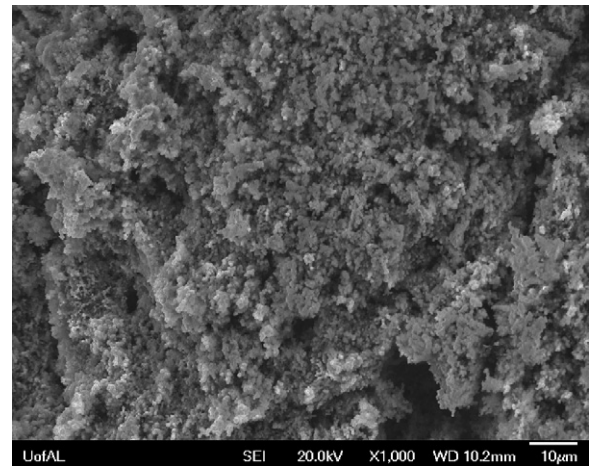

Fig. 2. Microstructure of the electrodeposited HCP nickel.

patterns of the electrodeposited nickel from $NiCl_2 \cdot 6H_2O$ and $NiCl_2$, it is evident that the crystallinity decreases with increase in moisture in nickel chloride. The microstructure of the electrodeposited HCP nickel is shown in Fig. 2. The SEM shows the formation of nodular nickel structure. The SEM also shows the presence of a large number of pores which might be due to the growth characteristics of nickel nuclei during the electrodeposition process.

The DTA of the HCP nickel electrodeposited from $NiCl_2$-EmimCl and $NiCl_2 \cdot 6H_2O$-EmimCl are compared in Figs. 3 and 4. A single exothermic peak is observed at 462 °C in Fig. 3 which corresponds to the phase transformation from HCP nickel to FCC structure. The XRD of the sample after the DTA experiment confirmed FCC nickel phase. Since HCP nickel forms due to dissolution of H_2 [20], H_2 evolves during phase transformation. The TGA analysis along with gas chromatography carried out by Midwest Microlab laboratory confirmed the evolution for hydrogen during phase transformation. Electrodeposited Ni showed 1.2 wt.% hydrogen. DTA of electrodeposited HCP nickel from $NiCl_2 \cdot 6H_2O$-EmimCl shows two exothermic peaks (Fig. 4), one at 291 °C and another one at 459 °C. The corresponding TGA curve in Fig. 4 shows two weight loss stages. First one commences at around 240 °C and continues until 320 °C and other one starts at around 445 °C and continues till 500 °C. TGA along with gas chromatography carried out by Midwest Microlab showed that the first and second peaks are associated with the removal of
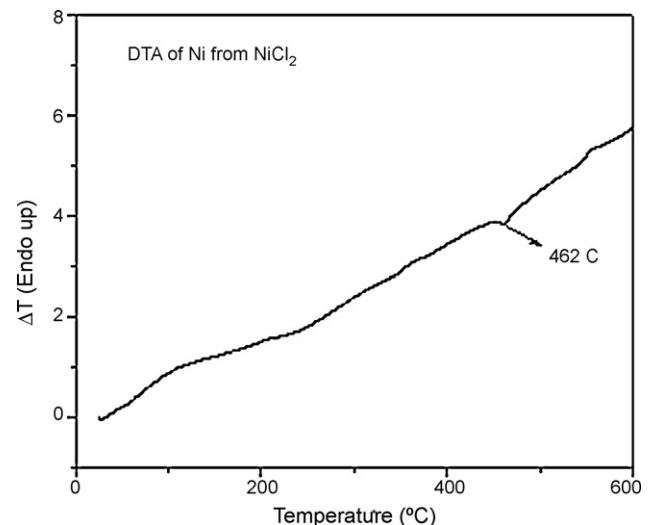

Fig. 1. Comparison of electrodeposited HCP nickel with standard ICDD pattern.

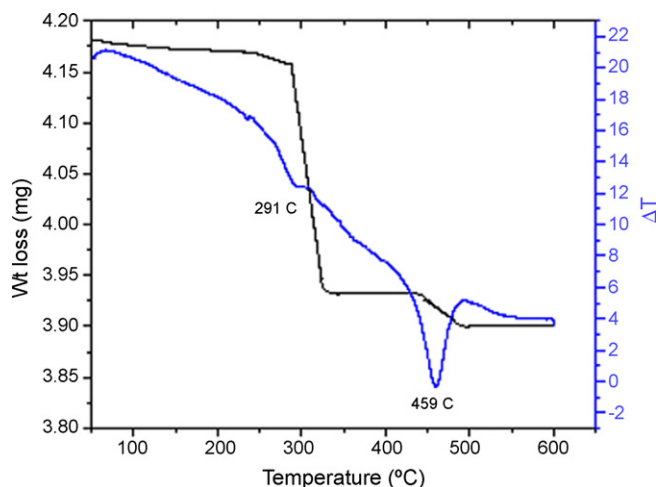Fig. 3. DTA of the nickel electrodeposited from $NiCl_2 \cdot$EmimCl.

Fig. 4. TGA and DTA of the electrodeposited nickel from $NiCl_2 \cdot 6H_2O \cdot EmimCl$.

organic compounds and H_2, respectively. The amount of carbon and hydrogen released at 291 °C was 7.1 and 0.3 wt.%, respectively. Since ionic liquid is the only source of organic compound, carbon in nickel indicates decomposition of ionic liquid at high concentration of water. It has been previously reported that the presence of water decreases the electrochemical window of the ionic liquid [21] and therefore on applying −2.0 V in $NiCl_2 \cdot 6H_2O$-Emimcl, the ionic liquid decomposes. The second peak in the DTA represents the phase transformation of HCP nickel to FCC phase. 0.7% H_2 was released during this transformation. Since 0.3% hydrogen came out at 291 °C, total hydrogen dissolved in nickel electrodeposited from $NiCl_2 \cdot 6H_2O$ was 1%. It is interesting to note that although $NiCl_2 \cdot 6H_2O$-EmmiCl melt has higher percentage of water compared to that of $NiCl_2$-EmmiCl melt, electrodeposited Ni from the former had lower percentage of hydrogen. Comparing Figs. 3 and 4, a difference of 3 °C in the phase transformation temperature from HCP nickel to FCC is observed which might be due to the non-identical crystal structure of the electrodeposited HCP nickel from the two different nickel chloride salts.

Since the purpose of this work was to establish the possibility of electrochemically storing hydrogen in nickel, no attempt has been made to study the kinetics of hydrogen evolution.

FCC nickel produced after the release of hydrogen from the HCP nickel can be recycled by introducing it back in the ionic liquid melt and electrodepositing HCP nickel. It is anticipated that such electrochemical technique can be used to synthesize alloys such as $LaNi_5$ at low temperatures and store hydrogen in the material during the electrolysis process as demonstrated in this communication.

4. Conclusions

1. Hydrogen of 1–1.2 wt.% can be stored in HCP nickel. The electrochemical process provides a simple technique for simultaneous hydrogen generation and storage during the electrodeposition of HCP nickel using ionic liquids.
2. HCP nickel transforms to stable FCC structure at 459–462 °C by releasing hydrogen.
3. Higher concentration of water in ionic liquid does not lead to higher concentration of hydrogen in HCP nickel.

Acknowledgement

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