

New Ball-Milled Metal Hydride Electrode for Rechargeable Batteries

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Abstract

A new type of anode materials in form of nanocrystalline composite powders has been developed that offers the potential for dramatically improved discharge capacity and initial activation rate. The composites are synthesized by ball milling of two components - a major component (basic component) having high hydrogen capacity and a minor component (surface activator) with good electrocatalytic activity. The capacity increase observed by ball milling with surface activator. The ball-milled composite materials are easier to activate than the non ball-milled basic component.

1. Introduction

Rechargeable batteries based on metal

hydrides as the anode material with, say, nickel hydroxide as the counter electrode, have been received a lot of attention in the

last ten years and have begun to penetrate the market in a significant way^[1-4].

In order to use metal hydrides in rechargeable batteries, the following performances are essential for hydride materials :

- a high electrochemical capacity, i.e. the ability to absorb reversibly large amounts of hydrogen at room temperature,
- a high resistance to corrosion in alkaline solution for long cycling life,
- high electrocatalytic activity for the electrochemical reduction of water (high charge rates),
- high attainable discharge rates
- high energy density
- easy activation

For a given anode material, it is difficult to obtain simultaneously all the performances mentioned above. Generally, the procedures used to improve the metal hydride electrode characteristics optimize one property, while sacrificing another. Various approaches have been employed to obtain metal hydride electrodes with appropriate performances, like multi alloying, surface treatments, microencapsulation, synthesis of two phase alloys^[5-11].

This study is intended to develop new ball-milled hydride electrode materials with surface activators for superior performances of nickel-metal hydride rechargeable batteries. A new type of composite hydride electrode materials is synthesized by ball milling hydrogen absorbing components with surface

activator : a major component (component 1), with good hydrogen storage properties and a minor component (component 2), used as "surface activator", i.e. having good electro-catalytic activity.

The main directions of this research are developing and testing new ball-milled anode materials in form of nanocrystalline composite powders. As a major component, two types of intermetallic compounds are selected :

- (1) AB₅ type : LaNi₄Fe_{0.85}Al_{0.15} + 0, 5, 10, 15% excess La
- (2) AB₂ type : Zr_{0.9}Ti_{0.1}Fe_{1.15}Cr_{0.85}

As surface activator, we have used Ni and LaNi₄Fe_{0.85}Al_{0.15} (10% excess La)

2. Experimental

Battery cycling experiments have been performed with AB₂- and AB₅-type composite hydride materials using surface activator. The alloys of component 1 and 2 were prepared in arc melting the pure metals with appropriate compositions under argon atmosphere. These alloys were pulverized mechanically to 75 μm. The major components were mixed with surface activators, 10% Ni and LaNi₄Fe_{0.85}Al_{0.15} (10% excess La), and

the resultant mixture was then introduced together into a SPEX-8000 vibrator ball mill. After sealing with an O-ring, the mixture was subjected to a ball milling treatment for

1 hour at room temperature. All composite materials were sieved through a 300 mesh screen after ball milling. Crystallographic characterizations of the alloys were carried out by x-ray diffraction before and after ball milling.

The composite powders were mixed with electrolytic copper powder, and the resultant mixture was compressed. The cycling experiments were then carried out with Ni(OH)₂/Ni(OOH) cathodes in 6M KOH. The charging was conducted using the current rate of 100 mA/g(active material) and a "flash" (short circuit) was applied every half an hour, in order to discharge the impurities deposited on the negative electrode (mainly Cd from the commercial positive Ni counter-electrode). The experiments were made in flooded conditions in open cells.

3. Results and Discussions

The XRD patterns for LaNi_{4.0}Fe_{0.85}Al_{0.15} (10% excess La) are shown in Fig. 1(a)-(b) before and after ball milling for 1 hour. As shown in figure, the peaks of alloy decreased greatly in intensity and broadened (enlargement of the lines). This profile indicated that the structure of this alloy was transformed to a nanocrystalline. A line fitting program was used to get the grain size; it was found that the grains were 20-40nm for alloy ball-milled for 1 hour.

The charge-discharge characterizations of

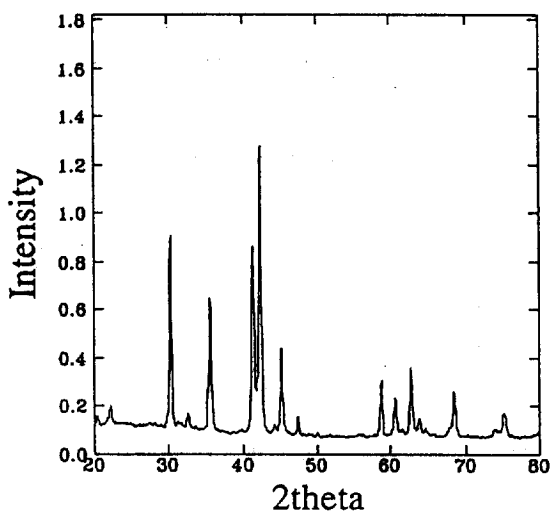


Fig. 1(a) XRD pattern of LaNi_{4.0}Fe_{0.85}Al_{0.15} (10% excess La)

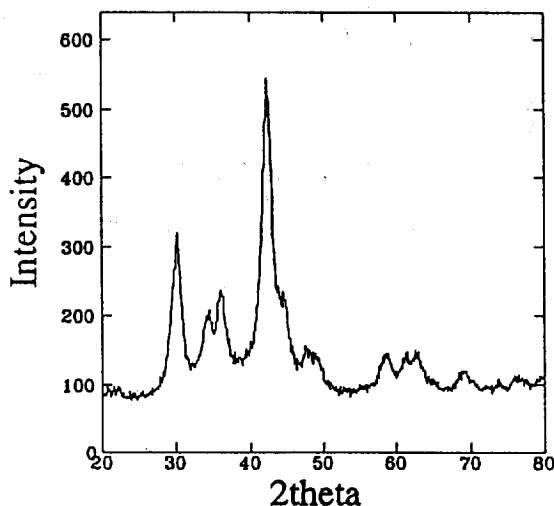


Fig. 1(b) XRD pattern of LaNi_{4.0}Fe_{0.85}Al_{0.15} (10% excess La) ball milled for 1h

ball-milled LaNi_{4.0}Fe_{0.85}Al_{0.15} alloy with 0, 5, 10, 15% excess La were investigated and their discharge trends with various excess

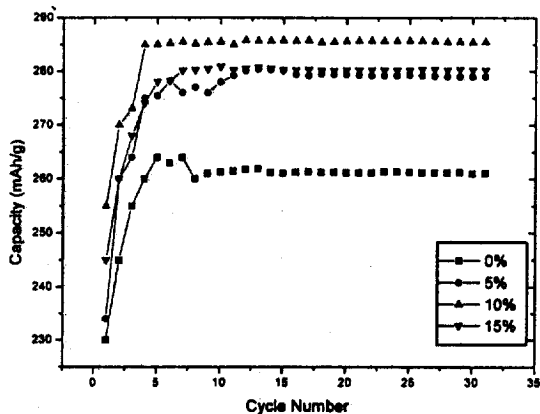


Fig. 2 Discharge capacity vs number of cycles for $\text{LaNi}_{4.0}\text{Fe}_{0.85}\text{Al}_{0.15}$ (0, 5, 10 and 15% excess La) ball milled for 1h

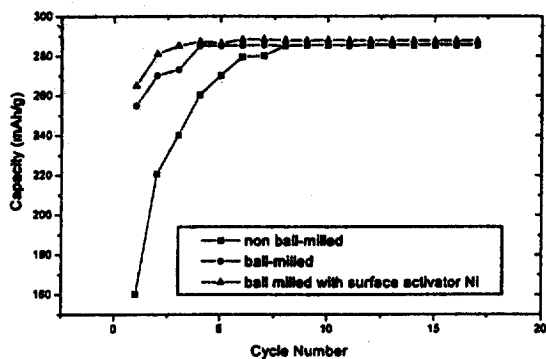


Fig. 3 Discharge capacity vs number of cycles for $\text{LaNi}_{4.0}\text{Fe}_{0.85}\text{Al}_{0.15}$ (10% excess La)

La are shown in Fig. 2 As shown in figure, it was found that the capacity increased with increasing excess La within 10% excess La. However, the capacity decreased when the excess La is higher than 10%. From the results, it was suggested that about 10% excess La should be added for the best discharge capacity.

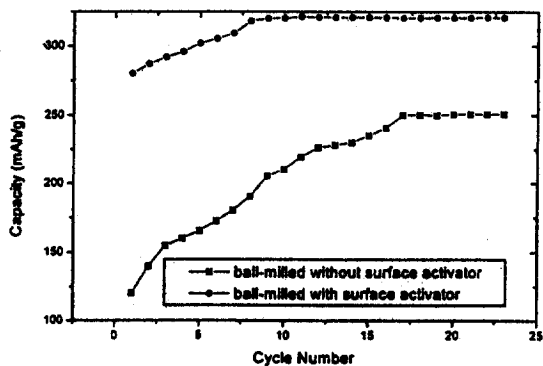


Fig. 4 Discharge capacity vs number of cycles for $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Fe}_{1.15}\text{Cr}_{0.85}$ ball milled with and without surface activator

Fig. 3 shows the discharge capacities of ball-milled and non ball-milled $\text{LaNi}_4\text{Fe}_{0.85}\text{Al}_{0.15}$ alloy (10% excess La) with and without Ni powder. The initial activation increased by ball milling whereas the capacity is almost same between ball-milled and non ball-milled electrodes. On the other hand, the capacity for ball-milled electrode with Ni powder is little high compared with those of non ball-milled and ball-milled electrodes without Ni powder. From the results, it suggests that the ball milling treatment with a surface activator is an effective way to improve the discharge capability of a anode material

The investigation of the electrochemical behavior of the basic component, $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Fe}_{1.15}\text{Cr}_{0.85}$ and composite powders with surface activator, $\text{LaNi}_4\text{Fe}_{0.85}\text{Al}_{0.15}$ alloy (10% excess La) was obtained in charge-discharge experiments. The results are shown in Fig. 4 From the results it was

found that the capacity for composite electrode, is higher than that of basic component electrode and the initial activation is much easy compared with basic component electrode. The improvement in discharge capacity and the easy activation behavior seems to be caused by the increase of fresh surface area during ball milling and by coating basic component with surface activator.

4. Conclusions

A new class of composite hydride anode materials have been proposed for rechargeable batteries. The composites were prepared by ball milling of two components (basic component + surface activator). From the results of electrochemical properties, it was found that the initial activation was enhanced, and the discharge capacity increased by ball milling with surface activator, Ni and $\text{LaNi}_{4.0}\text{Fe}_{0.85}\text{Al}_{0.15}$ (10% excess La).

The electrochemical properties of ball-milled $\text{LaNi}_{4.0}\text{Fe}_{0.85}\text{Al}_{0.15}$ alloy were investigated with various amount of excess La. The results showed that the discharge capacity increased within 10% of excess La. But it decreased, if excess La is higher than 10%.

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