

Effect of the Cerium Oxide (CeO_2) on the Structural and Electrochemical Properties of the LaNi_5Ce Metal Hydride Anode

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Abstract. One of negative electrode, AB_5 -type alloy electrodes, have been extensively studied and applied in rechargeable Ni-MH batteries due to their excellent electrochemical characteristics. Some researchers have found that addition of rare earth oxides (La, Ce, Pr, Er, Tm, Yb) to AB_5 -type alloy (MH) electrode improves battery performance significantly. Cerium Oxide (CeO_2) is a light rare earth oxide is widely obtained from the processing of tailings in mining activities. During this time, there is still little data for research applications of cerium oxide for electrode materials. In this paper, the effects of adding CeO_2 on the performance metal hydride electrode were investigated. In order to study the effects of CeO_2 on the performance of anode material, 1%, 2%, and 3% of weight ratio CeO_2 was mixed to LaNi_5 as an negative electrode. The powder mixtures were mechanically milled at a speed of rpm 240 for 2 hours using ball mill. The powder mixtures were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). Electrochemical characteristics were measured using electrochemical impedance spectroscopy (EIS). The powder mixing showed the presence of Ce atom substitution into LaNi_5 structures that affect the electrochemical properties of the material. The addition of cerium oxide at LaNi_5 increase of the value of impedance. However, the addition of the value of impedance at 1% CeO_2 is not significant when compared with the addition of 2% and 3% CeO_2 that actually make the electrochemical properties of LaNi_5 worst. Although the addition of 1% CeO_2 also slightly increases the impedance value of LaNi_5 , but the addition of 1% CeO_2 showed increase the corrosion resistance than without the addition of CeO_2 and the addition of 2% and 3% CeO_2 .

1. Introduction

Nickel-metal hydride (Ni-MH) batteries have been widely used for both consumer and industrial applications due to their advantages such as flexible design, excellent power, long cycle life and environmental friendliness. Although Ni-MH batteries are commercially available, their performance still needs to be improved by further research. It is well known that the capability of negative electrode is one of the key issues for Ni-MH batteries, depending on active materials and the preparation method of negative electrode. One of negative electrode, AB_5 -type alloy electrodes, have been extensively studied and applied in rechargeable Ni-MH batteries due to their excellent electrochemical



characteristics. Some researchers have found that addition of rare earth oxides (La, Ce, Pr, Er, Tm, Yb) to AB₅-type alloy (MH) electrode improves battery performance significantly [1-3].

Cerium Oxide (CeO₂) is a light rare earth oxide is widely obtained from the processing of tailings in mining activities. In Indonesia, mineral containing rare earth metal elements (La, Ce, Nd, Y) are as associated minerals in mineral gold, alluvial tin, bauxite, and copper. Despite the potential of rare earth metals in Indonesia is quite high, but during this time, there is still little data for research applications of cerium oxide for electrode materials. In this paper, the effects of adding CeO₂ on the performance metal hydride electrode were investigated. In order to study the effects of CeO₂ on the performance of anode material, 1%, 2%, and 3% of weight ratio CeO₂ was mixed to LaNi₅ as an negative electrode.

2. Experiment Detail

Hydrogen storage grade LaNi₅ samples from Aldrich were used for the study. The powder LaNi₅ then mixtures with 1%, 2%, and 3% of weight ratio powder CeO₂ and alcohol to complete the mixture. The powder mixture then was mechanically milled using RETSCH ball mill at a speed of rpm 240 with a 5 steel ball. Samples were prepared with milling time 2 hours and 30 min pause-time to avoid the heating of the sample during the milling process. The powder mixtures were drying with oven drying at 80°C for 17 hours.

The powder mixtures were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). Electrochemical characteristics were measured using electrochemical impedance spectroscopy (EIS) in 6 M KOH aqueous solution using a three-electrode cell. The working electrode was composed of 2 g composite powder and 0.1 ml PEG, and then was cold pressed into a pellet of 15 mm in diameter under 10 Metric Ton. Carbon was the counter electrode, and Hg/HgCl was the reference electrode. Electrochemical impedance spectroscopy (EIS) studies of the electrodes were performed in a frequency range between 5 mHz – 100 kHz. Tafel polarization curves were measured at a scanning rate of 1 mV/s from -1.5 to -0.5 V.

3. Result and Discussion

From the results of phase identification by XRD Figure 1, the addition of CeO₂ concentration in the powder mixture LaNi₅ would changes in the peak of the phase. The dominant phase before and after the addition of the oxide to LaNi₅ look slightly formed a new peak. The addition of CeO₂ concentration showed peaks that began appearing on the addition of 1%, 2%, or 3%. Although the peak of CeO₂ which appears not very significant between each concentration is added, but the peak of CeO₂ that appears with the addition of 1%, 2%, and 3% showed the presence of a new phase.

The formation of a new phase identified by XRD analysis, reinforced by the analysis using method GSAS. Table 1 shows the results of the analysis phase identified and size of cell volume with variations in concentration of 1%, 2%, and 3% CeO₂ using methods GSAS. With GSAS method is known that there are atom substitution La and Ce. The existence of substitution atoms La and Ce increases with increasing concentration of CeO₂ added. La and Ce atom substitution also affect the cell volume. Cell volume increased with the addition of oxide concentration of 1% and the cell volume decreases with the addition of oxide concentration of 2% and 3%. Contraction of volume cell indicates the size of the interstitial space for the hydrogen atoms to the alloy. This will cause the process of diffusion of hydrogen atoms on the surface of the alloy becomes more difficult [4].

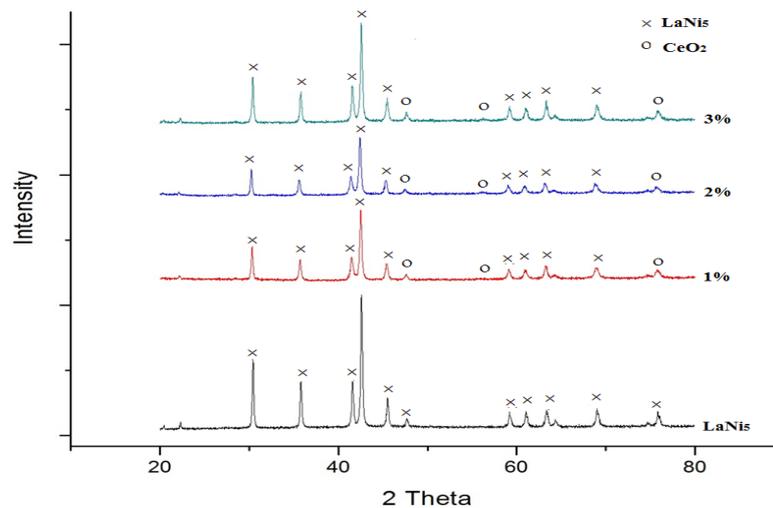


Figure 1. The results of XRD analysis of the powder mixture LaNi_5 and CeO_2 with various concentration of 1%, 2%, and 3% CeO_2 .

Table 1. Results of the analysis phase identified and size of cell volume with variations in the concentration of 1%, 2%, and 3% CeO_2 using GSAS methods.

Sample	a	b	c	Volume Cell	Fasa Identifikasi
LaNi_5	5.014567	5.014567	3.98548	86.792	LaNi_5
+ 1% CeO_2	5.021173	5.021173	3.98548	87.157	$\text{La}_{0.99}\text{Ce}_{0.01}\text{Ni}_{4.922}$
+ 2% CeO_2	5.020298	5.020298	3.990819	87.107	$\text{La}_{0.98}\text{Ce}_{0.02}\text{Ni}_{5.202}$
+ 3% CeO_2	5.013347	5.013347	3.986693	86.776	$\text{La}_{0.97}\text{Ce}_{0.03}\text{Ni}_{5.562}$

Analysis of the morphology of the SEM is intended to look at the effect of the milling process of the morphology of the particles of the powder. LaNi_5 particle morphology before and after the addition of cerium oxide concentration of 1%, 2%, and 3% are shown in Figure 2. Observations made on 500x magnification. In general, from the observation with SEM, reflecting the particle size reduction of about 50 μm to 5-10 μm from before the addition and after the addition of cerium oxide concentration in all variations. Particle size reduction occurs because of the process of mixing with cerium oxide (CeO_2) using the method of milling for 2 hours at 240 rpm SEM results showed that the particles spread evenly on all additional concentration. This shows that the process of mixing with milling method successfully leveled the cerium oxide particles in LaNi_5 .

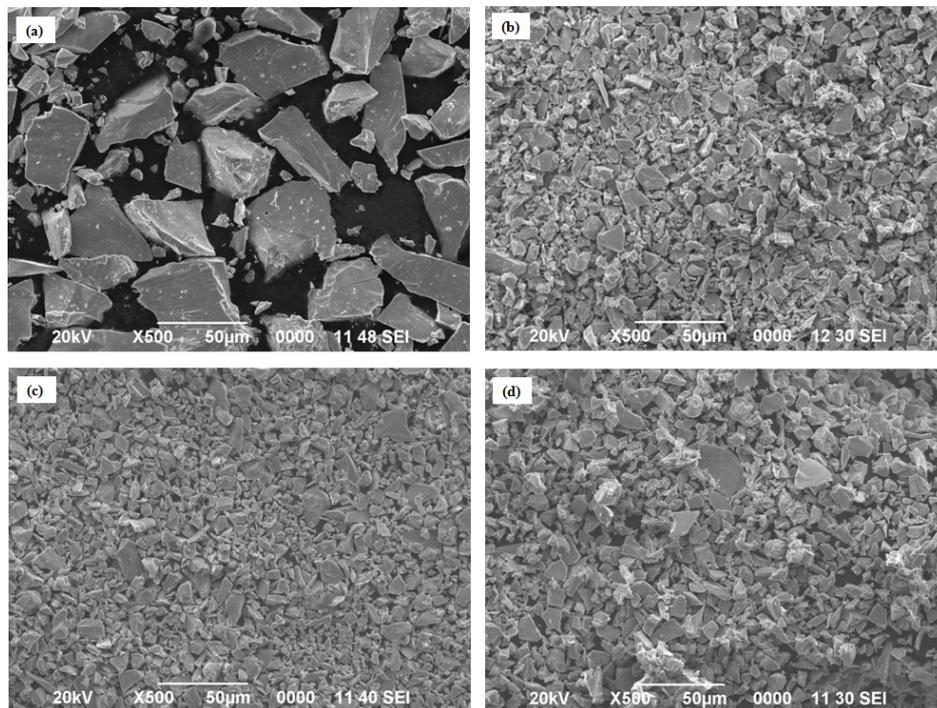


Figure 2. The morphology of the powder LaNi_5 and mixture LaNi_5 (a) with variation CeO_2 concentration (b) 1%, (c) 2% and (d) 3%

Profile EIS shown from measurements LaNi_5 material with varying concentrations of cerium oxide is shown in Figure 3. It looks a diffusion process in areas with high frequency which is then followed by the formation of an arc at a frequency being in every variation of oxide concentration. The addition of oxide concentration in LaNi_5 , will increase large arc pattern. The profile area that forms the greater arc at a frequency of charge-transfer medium indicates that the greater the resistance. The formation of small semicircle at low frequency area indicates the resistance area between the current collector material / pellet alloy powder [5]. In the measurement results, profile EIS of LaNi_5 material with the addition of 1% CeO_2 which showed the formation of small semicircle at low frequency area. This shows that the material LaNi_5 with the addition of 1% CeO_2 can be used as an anode material.

As is known from previous studies, the addition of rare earth metal oxides into metal hydride electrode will improve battery performance which is to reduce the rate of corrosion and increase the longevity of battery life [1-3]. To determine the corrosion rate of a material can be calculated by using the polarization curves. Linear polarization curves of LaNi_5 with CeO_2 concentration variation shown in Figure 4. The polarization curves show a pattern of increasing current density (I_o) when given in addition to the concentration of cerium oxide material LaNi_5 .

Calculation shows the highest E_{corr} was -0.6432 V which when added 1% cerium oxide. And the lowest E_{corr} -1.0411 V when added 3% cerium oxide. The greater value of E_{corr} indicates better corrosion resistance on the electrode and can improve the cycle stability of the electrode [6].

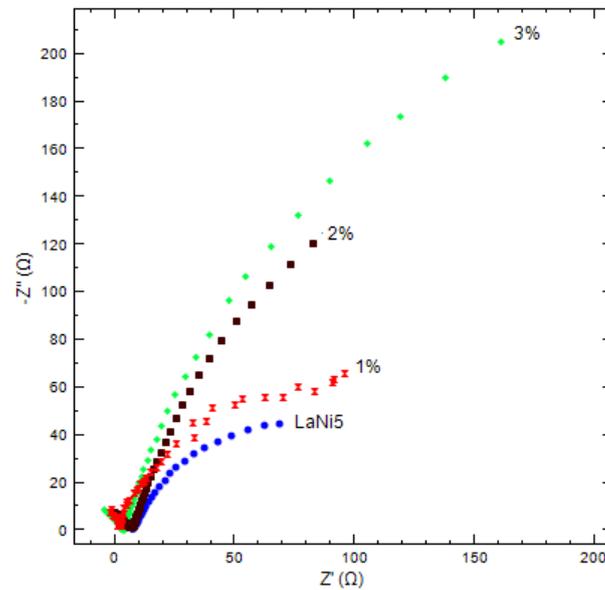


Figure 3. AC impedance spectra at room temperature of LaNi_5 with varying concentrations of cerium oxide.

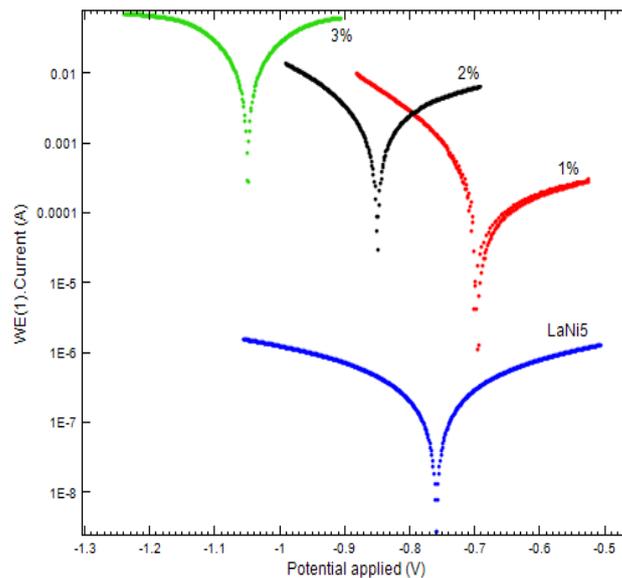


Figure 4. Linear Polarization curves of LaNi_5 with variations CeO_2 concentration.

4. Conclusion

The powder mixing showed the presence of Ce atom substitution into LaNi_5 structures that affect the amount of cell volume. The amount of cell volume affects the electrochemical properties of the material. In general, the new phases are formed with addition of CeO_2 concentration were $\text{La}_{1-x}\text{Ce}_x\text{Ni}_5$ ($x = 0.01 - 0.03$). The addition of cerium oxide at LaNi_5 shows the increase of the value of impedance. However, the addition of the value of impedance at 1% CeO_2 is not significant when compared with the addition of 2% and 3% CeO_2 that actually make the electrochemical properties of LaNi_5 worse. It is shown by impedance value that is higher on the addition of 2% and 3% CeO_2 . Although the addition of 1% CeO_2 also slightly increases the impedance value of LaNi_5 , but from the polarization curve, the

addition of 1% CeO₂ showed increase the corrosion resistance than without the addition of CeO₂ and the addition of 2% and 3% CeO₂

Acknowledgments

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