

Preparation and hydrogen storage properties of $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ as the negative electrode of a hydrogen battery

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The high-temperature proton-conducting oxide, $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Ru}_{0.05}\text{O}_{3-\delta}$, was applied as the anode of a hydrogen battery. The electrochemical charge/discharge properties were investigated, by a conventional three-electrode cell with a KOH solution, as a function C-rate, cycle number, and nickel contents. The relatively low-charging current for an oxide electrode, compared with a metal electrode, was discovered due to the low electronic conducting properties of the oxide electrode. The degradation of charge capacities of the oxide electrode was also observed due to the evolution of hydrogen gas during charging, which may have blocked the contact area between the electrode and electrolyte, leading to a decrease in active electrode reaction areas. Furthermore, the oxide electrode displayed systematic degradation in discharge capacities as the number of cycles was increased.

Key words: Perovskite-type oxide, Hydrogen storage, Negative electrode.

Introduction

Because hydrogen batteries have several advantages (such as higher energy density, durability against overcharge and over-discharge, compatibility with a nickel-cadmium battery, cleanliness, and freedom from poisonous heavy metals) over conventional secondary batteries, nickel/metal-hydride (Ni-MH) batteries have been considered a viable option for reducing the dependence on fossil fuels and enhancing energy efficiency [1-5]. Until recently, mischmetal-based AB_5 type alloys [6, 7], Zr-based laves alloys [8], and Mg-based alloys [9-10] have been employed as negative electrode materials. However, none of these is currently favoured, because the reversible capacities of these materials are about 300 mAhg^{-1} with the most frequently used material being an AB_5 -type negative electrode, which is still insufficient for portable electric devices and vehicles [11].

Recently, researchers have reported possible applications of proton-conducting oxides for a new negative electrode of the Ni-H battery. Esaka et. al [12] initially reported the possibility of $\text{ACe}_{1-x}\text{M}_x\text{O}_{3-d}$ ($\text{A} = \text{Sr}, \text{Ba}$, $\text{M} = \text{rare earth elements}$) as negative electrodes of the Ni-H battery, as a function of the B-site acceptor dopant concentration. The variation of discharge capacities against acceptor dopant concentration showed a maximum at 0.05 mol %. The highest discharge capacity (119 mAhg^{-1}) was observed at the

low current density of 9.25 mA g^{-1} for the $\text{BaCe}_{0.95}\text{Nd}_{0.05}\text{O}_{3-\delta}$. However, the considerable hydrogen storage properties of doped proton-conducting perovskite do not follow the general trend of hydrogenation [13, 14]. The overall charge capacity and terminal voltage of the oxide anode may be influenced by the ionization potential of the B-site cation, rather than by the basicity of the system. Therefore, a wider range of composition and electrochemical analyses of proton-conducting oxides for the hydrogen battery application should be performed.

In this study, $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ proton-conducting oxide was selected because the Zr-rich perovskites normally show chemical stability against the Ce-rich phase [15, 16]. As an acceptor dopant, Y was selected in order to introduce oxygen vacancies into the structure, and Rb was added to enhance the catalytic effect of the oxide. The electrochemical charge/discharge properties were investigated as functions of C-rate, cycle number, and nickel content.

Experimental

Polycrystalline $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ samples were prepared by conventional solid-state reactions. High-purity oxide powders of BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 (all 99.9% purity and sourced from Alfa Aesar) and Rb_2CO_3 (99.8%, Alfa Aesa) were mixed, ground in a ball mill with stabilized zirconia balls, and calcined at 1773 K, for 20 h in air. The calcined powder was then planetary ball-milled with stabilized zirconia balls for 4 h, at 200 rpm and sieved by 325 mesh ($45 \mu\text{m}$). The powders obtained were characterized by X-ray diffraction (XRD; D/MAX Ultima III, Rigaku, Japan)

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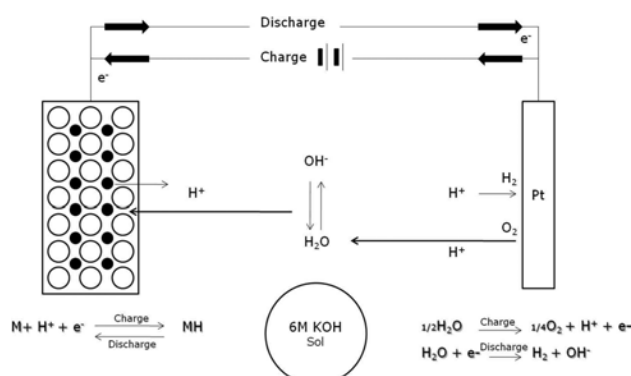


Fig. 1. Schematic view of charge/discharge experiment.

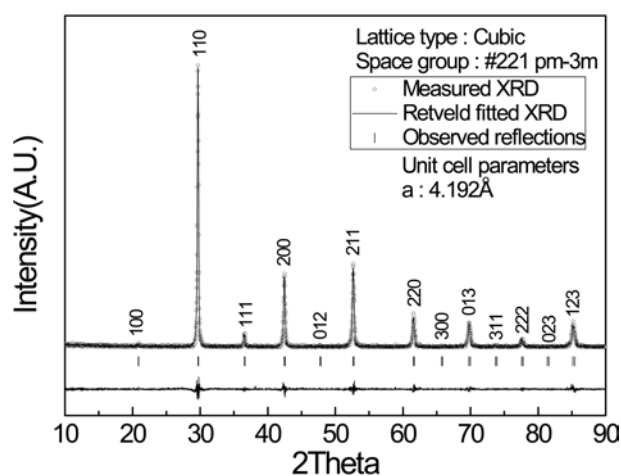


Fig. 2. Room-temperature X-ray diffraction (XRD) patterns of $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ calcined at 1773 K in air for 20 h.

equipped with a Cu target X-ray tube at a scan rate of $2^\circ\text{minute}^{-1}$ between scanning angles of (2θ) 10° and 90° .

The powders were used for electrochemical testing. Hydrogen charge and discharge performance of each sample was estimated with a three-electrode electrochemical cell. In order to make a test electrode, as-prepared powders, which are generally inactive with hydrogen, were mixed with nickel powder as a current distributor; and ball-milled in a zirconia pot for 20 h. Thereafter, a small amount of aqueous solution with 6% PVA was added as a binder and the resultant slurry was pasted onto a porous nickel gauze substrate ($1\text{ cm} \times 1\text{ cm}$). The electrochemical measurements were performed by a three-electrode cell consisting of a working electrode (sample), counter electrode (Pt), and reference electrode (Hg/HgO). The electrolyte was a 6 M KOH solution. The charge/discharge currents were determined by the sample weight and measured by a galvanostatic method (Wonatech, WBCS 3000). The charging rate was varied, with 0.4 mA/g for 25 h, 0.7 mA for 15 h, and 1 mA/g for 10 h, and then discharged at the same current density. The schematic experimental design for the half reaction is shown in Fig. 1. The cut-off voltage for discharge was -0.01 V vs. Hg/HgO.

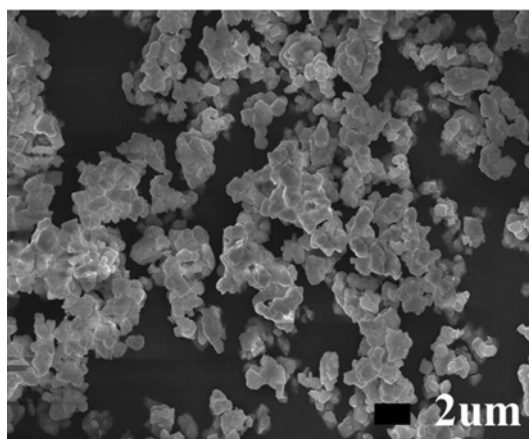


Fig. 3. Microstructure images of $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ calcined at 1773 K in air for 20 h.

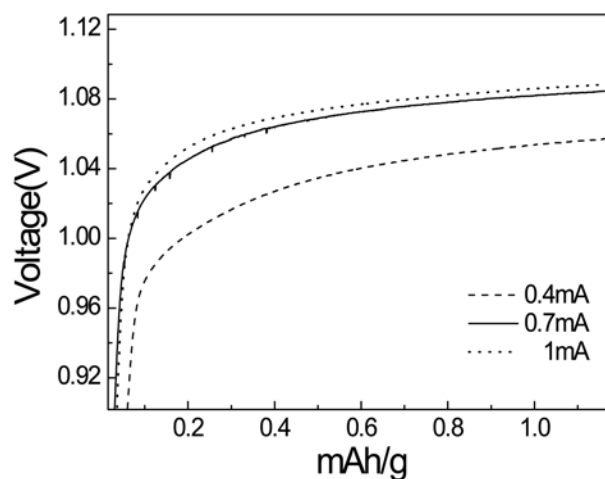


Fig. 4. Charge curves of $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ electrode at various charging currents, at room-temperature.

Results and Discussion

The XRD patterns obtained were refined using the Full-Prof program according to the Rietveld method, as shown in Fig. 2. Although the results of the line profiling analysis may not be completely reliable due to the relatively fast scan rate ($1^\circ\text{minute}^{-1}$), no peaks were detected for any other planes, indicating the high purity of the product. The refined cubic perovskite unit cell parameters for $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ at ambient temperature were 4.192 Å . A scanning electron microscope (SEM; Shimadzu, SS-550) image of the calcined powder is shown in Fig. 3 and reveals well-distributed powders around 1 μm in diameter.

The charging properties of the anode $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ for a hydrogen battery were examined as a function of the charging rate, with a cutoff voltage of 0.01 V . Due to the low electronic conducting properties of the oxide anode, a low current rate, down to 0.4 mA/g , was applied with 1.5 wt. % carbon black to enhance the electronic conductivity. Fig. 4 shows typical charging curves, with various

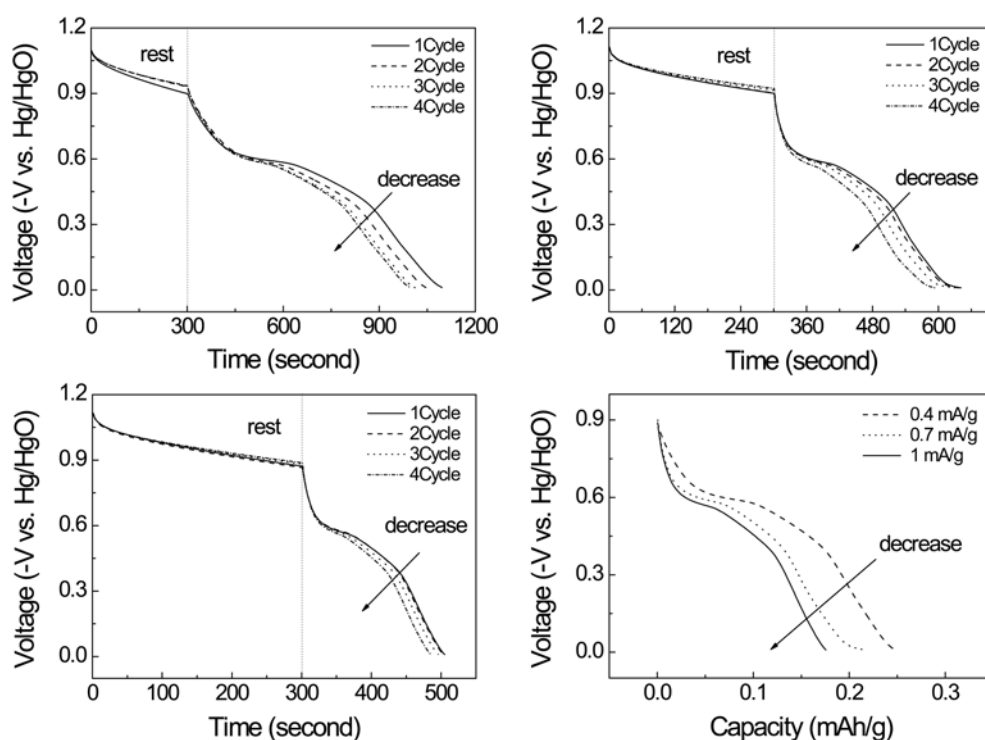


Fig. 5. Discharge curves of $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ (a) 0.4 mA/g, (b) 0.7 mA/g, (c) 0.1 mA/g, and (d) comparison with various charge currents.

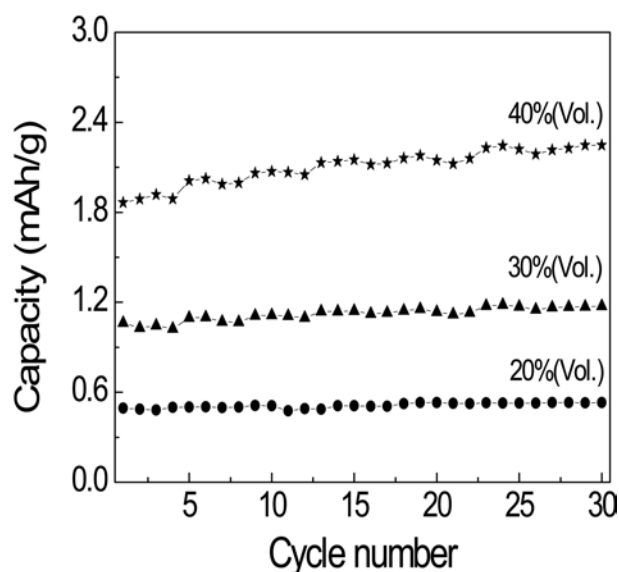


Fig. 6. Effect of discharge capacities of the nickel content on cycling.

charging rates, showing low a voltage with a lower charging current due to the parasite electrode reaction of electrolysis. The ultimate charging current for the oxide electrode was relatively low compared with that of the metal electrode [17, 18]. The residual current may reduce the proton to evolve hydrogen gas, which would decrease the contact area between the electrode and electrolyte. A decrease in the active electrode reaction areas may cause an increase in resistance, followed by the increase in voltage.

The discharge capacities of the $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ anode were measured after 5 minute of rest time. As shown in Fig. 5, the electrode showed systematic degradation in discharge capacities when the number of cycles was increased. With a fixed discharging condition, the electrode with a low current charging rate shows a relatively higher discharging capacity, as expected from Fig. 4. The small discharging capacities, when compared to those in the previous literature, may be understood by the difference in composition: a Zr-rich perovskite composition may not be suitable for hydrogen charging because the fixed valence of the B-site cation does not allow the proton to be incorporated into the oxide while maintaining charge-neutrality [19]. Therefore, by enhancing the electronic conductivity of the oxide electrode, one may enhance the discharge capacity of the oxide electrode while enhancing the time delay regarding reaching the hydrogen evolution voltage. One would achieve this by uniformly distributing the current over the well-connected electrode reaction active area. It is also worth noting that, like with a Ni-MH battery using a hydrogen storage alloy as a negative electrode [17], a clear potential plateau regime during discharging was observed around 0.6 V.

Fig. 6 shows the cycle stability at various nickel contents under a charge/discharge current density of 0.4 mA/g. The cycleability of $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ anode with nickel does not show any degradation when the number of cycles is increased. When the amount of nickel was greater than 20 wt. %, the discharge capacity appeared to be improved not only in

the discharge capacity but also with regard to cycleability. The increase in discharge capacity with a higher nickel content should be the direct effect of the enhanced electronic conductivity of the electrode, helping the current distribution along the enlarged active electrode area. However, the present results of Zr-rich perovskite proton conducting oxides may be unfavorable to the application in the anode of a hydrogen battery. It is fair to say that the overall low electrode properties of the $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$ anode may be influenced by the low electronic conductivity so that a higher electronic conducting oxide should be developed for the anode application of a hydrogen battery.

Conclusion

The high-temperature proton conducting oxide, $\text{BaZr}_{0.65}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Rb}_{0.05}\text{O}_{3-\delta}$, was applied as the anode of a hydrogen battery. The charge/discharge capacities were measured as a function of charge/discharge rates with different nickel contents. The relatively low charging current for the oxide electrode, compared with a metal electrode, is necessary due to the low electronic conducting properties of the oxide electrode. Gradual degradation in charge capacities were found due to the evolution of hydrogen gas during charging, which may block the contact area between the electrode and electrolyte and lead to a decrease in the active electrode reaction areas. The overall electrode properties of the oxide anode for a hydrogen battery should be enhanced by increasing their electrical conductivity.

Acknowledgements

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