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# Electrochemical properties and hydrogen storage mechanism of perovskite-type oxide $LaFeO_3$ as a negative electrode for Ni/MH batteries

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ABSTRACT

Perovskite-type oxide $LaFeO_3$ powder was prepared using a stearic acid combustion method. Its phase structure, electrochemical properties and hydrogen storage mechanism as negative electrodes for nickel/metal hydride (Ni/MH) batteries have been investigated systematically. The results of X-ray diffraction (XRD) analysis show that both the calcined powder and the charged/discharged samples after 10 cycles have orthorhombic structures. The discharge capacity, whose maximum value appeared at the first cycle, is 530.3 mA h $g^{-1}$ at 333 K and increases with an increase in temperature. The discharge capacity decreases distinctly during the first three cycles and then stays steady at about 80 mA h $g^{-1}$, 160 mA h $g^{-1}$ and 350 mA h $g^{-1}$ at 298 K, 313 K and 333 K, respectively. The hydrogen storage mechanism is studied by XRD, X-ray photoelectron spectroscopy (XPS) and mass spectrometry (MS), coupled with pressure–composition–temperature (PCT) methods. Hydrogen atoms may be intercalating into the oxide lattice and forming a homogeneous solid solution during the charging process.

## 1. Introduction

Nickel/metal hydride (Ni/MH) batteries have been widely studied due to their high capacities, fast charge and discharge capabilities, environment-friendly characteristics and long cyclic stability [1–4]. All of the traditional negative materials in Ni/MH batteries are hydrogen storage alloys, including $AB_5$ [5,6], $AB_2$ [7], AB [8], and Mg-based materials [9–11]. Although Ni/MH secondary batteries with $AB_5$-type hydrogen storage alloys as negative electrodes have been widely applied in portable electronic devices, hand tools and vehicles, the reversible capacities of the alloys are only about 300 mA h $g^{-1}$. Moreover, the existence of Co in commercial $AB_5$-type electrodes increases the price a lot, which is unfavorable for electric vehicle applications, though it prevents the rapid decline in the alloy's hydrogen absorption capability during the charge–discharge cycling. A solid material that can store hydrogen reversibly with a capacity of 6.5 mass% and 62 kg $H_2$ $m^{-3}$ is the ideal target recommended by the U.S. Department of Energy (DOE) for automobile applications. Therefore, great effort has been invested in developing new types of hydrogen storage materials with improved electrochemical properties at lower cost than state-of-the-art negative electrodes [12–15]. Mandal et al. [16] have developed an unprecedented intake of hydrogen by $BaMnO_3$/Pt to the extent of 1.25 mass% at moderate temperatures (190–260 °C) at ambient pressure. However, little attention has been paid to the study of proton-conductive perovskite-type oxides despite their promising characteristics as negative electrode materials for Ni/MH secondary batteries. Esaka et al. [17] has proposed perovskite-type oxides $ACe_{1-x}M_xO_{3-\delta}$ (A = Sr or Ba, M = rare earth element) prepared by a conventional solid-state reaction method as innovative electrode materials for Ni/MH batteries. They deduced that the hydrogen storage mechanism is as follows:

$$BaCe^{(IV)}_{0.95}Nd_{0.05}O_{3-\delta}+xH_2O+xe^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} BaCe^{IV}_{0.95-x}Ce^{(III)}_xNd_{0.05}O_{3-\delta}H^{(I)}_x+xOH^- \qquad (1)$$

Unfortunately, the maximum discharge capacity of the $BaCeO_3$-based samples was only 119 mA h $g^{-1}$ at the discharge current density of 9.25 mA $g^{-1}$. Up to now, further research results have not been extensively reported. Recently our research team reported that the discharge capacities of the $ABO_3$-type perovskite oxide $La_{1-x}Sr_xFeO_3$ were more than 500 mAh $g^{-1}$ at a discharge current density of 31.25 mA $g^{-1}$ when the temperature rose to 333 K [18]. $ABO_3$-type perovskite oxides are superior to traditional hydrogen storage alloys because of their high hydrogen storage capacity, particularly at higher temperature, and at low cost. However, the electrochemical hydrogen storage mechanism of the perovskite oxide has yet to be elucidated.

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In addition, Ni/MH batteries are known to show the best performance between 20 °C and 40 °C. In the cells market, especially for vehicular applications and military devices, it is necessary for rechargeable batteries to work satisfactorily at relatively higher temperature range (from 40 °C to 80 °C). For example, for all batteries used in electric tools and electric or hybrid-electric vehicles (HEV), the ambient temperature might increase to 50 °C or even up to 80 °C, so the electrochemical performance of hydrogen storage alloys at high temperature draws people's attention. However, published literature on hydrogen storage alloy electrodes mainly focuses on electrochemical performance at approximate room temperature.

In this work, orthorhombic perovskite $LaFeO_3$ was prepared by a stearic acid combustion method, and its electrochemical properties at various temperatures and its hydrogen storage mechanism were investigated systematically.

## 2. Experimental

### 2.1. Sample preparation

$LaFeO_3$ was prepared by a stearic acid combustion method. All the reagents were analytical grade chemicals (98.5% in purity). Stearic acid ($C_{17}H_{35}COOH$) was used as both solvent and dispersant. The stearic acid was heated and melted, and then stoichiometric amounts of $La(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were mixed. The mixture was stirred by a magnetic mixer until a homogeneous sol-like solution was formed. The solution was ignited, and the resulting powder was calcined at 1123 K for 3 h in a muffle furnace in air.

### 2.2. Electrochemical measurements

Working electrodes were prepared by cold-pressing the mixture of the calcined powder (0.1 g) and carbonyl nickel powder with the weight ratio of 1:3 under 3.5 Mpa, forming a pellet with 10 mm in diameter and 1.5 mm in thickness was then formed. Electrochemical properties of each sample were tested in an open two-electrode electrochemical cell consisting of an MH electrode (working electrode) and a $Ni(OH)_2$/NiOOH electrode (counter and reference electrode), using a DC-5 computer-controlled battery testing instrument at 298 K, 313 K and 333 K, respectively. The charge/discharge tests were focused mainly on the electrochemical capacity and stability of the negative electrode. Thus, the capacity of the positive electrode plate (with an operating surface area of cal. 6 $cm^2$) was designed to be much higher than that of the negative one. Both electrodes were set in a 7 M KOH solution and charged at 125 mA $g^{-1}$ for 7 h, and then discharged to −0.6 V (vs. $Ni(OH)_2$/NiOOH) at 31.25 mA $g^{-1}$.

### 2.3. Sample characterization

To analyze the phase structures of the calcined powder and the charged/discharged samples, X-ray diffraction (XRD, Rigaku) studies were carried out on a D/max–rAX diffractometer with Cu Kα radiation. The XRD patterns were recorded between 20 °C and 80 °C with a step of 0.05° $s^{-1}$.

To identify the iron ion valence of the calcined powder and charged samples, XPS analysis was carried out on a XSAM800 X-ray photoelectron spectrometer (XPS, UK Kratos Co.) using Al Kα with a constant pass power of 12 kV × 15 mA. The binding energy data were corrected using the C1s peak at 285.0 eV. Data processing was performed with XPS peak program. After subtracting a Shirley background, the spectra were fitted with a least square fitting method from the Gauss/Lorentz (90/10) curves. Fe2p3/2 component of the Fe2p doublet was selected for binding energy quantification.

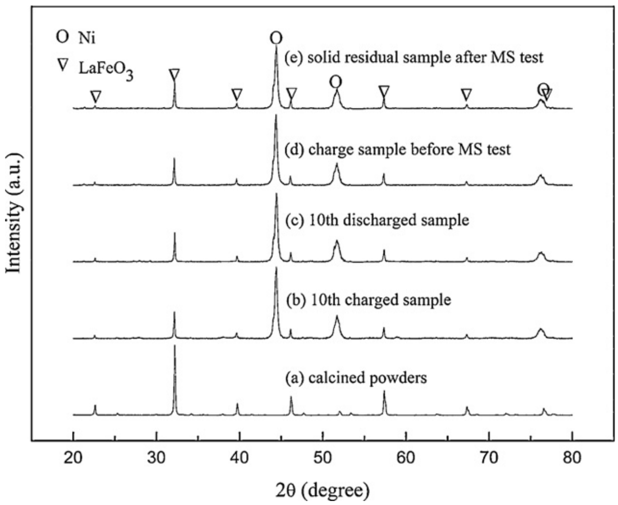

**Fig. 1.** XRD patterns of (a) the calcined oxide powder, (b) the 10th charged sample, (c) the 10th discharged sample, (d) the charged sample before MS test, (e) the solid residual sample after MS test.

MS instrument (MS, KYKY Technology Development Ltd) coupled with PCT equipment (Pro2000, PCT, Hy-energy Co.) was used to analyze the mixed gases released by the charged $LaFeO_3$ sample. The MS instrument was vacuumized to $5 \times 10^{-5}$ Pa and a background was obtained from the atmosphere in the PCT reactor. The charged samples were crushed into powder and put into a stainless steel reactor in the PCT equipment. The reactor was vacuumized for 5 min and then heated to 333 K, 423 K, 523 K and 623 K. The released gas was introduced into the MS for a final investigation.

To identify the iron ion, the electrolyte solution after 3 charge–discharge cycles was filtered and acidified by $H_2SO_4$, and then titrated using a 0.25 M $K_4Fe(CN)_6$ solution with the indicator of $KFe(Fe(CN)_6)$.

Cyclic voltammetry (CV) experiments were performed on an advanced electrochemical system, PARSTAT2273, with a conventional three-electrode cell at 50% depth of discharge (DOD). A sintered nickel electrode with a large capacity and an Hg/HgO electrode in 7 M KOH solution served as counter and reference electrodes, respectively. The potential scan rate was set to be 1 mV $s^{-1}$.

## 3. Results and discussion

### 3.1. Phase structure

The XRD patterns of the calcined powder, the charged/discharged samples and the sample before and after MS tests are all shown in Fig. 1. The diffraction peaks of all the samples are appointed to those of $LaFeO_3$ phase with an orthorhombic structure (JCPDS No: 88-0641), indicating that the phase structure remains stable during both the electrochemical and solid–gas reactions.

### 3.2. Electrochemical properties

Initial charge and discharge curves of the $LaFeO_3$ electrodes were plotted in Fig. 2. The charge curves show long and flat potential plateaus, possibly due to the formation of stable chemical bonds between hydrogen atoms and oxygen in the oxide. As reported by Mandal et al. [16], the perovskite structure favored formation of $OH^-$ ions with a reduction of $Mn^{4+}$ to $Mn^{3+}$ over the formation of Mn–H bonds. As the temperature increases from 298 K to 333 K, the charge potential plateau decreases from 1.5 V to 1.4 V. This phenomenon may be caused by a decrease in electrode polariza-