its phonon side band. A distortion of the TiO₆ octahedra (where the Mn⁺⁺ substitutes) in Gd₂MgTiO₆ is suggested.

The integrated luminescence intensity remains constant from \( T = 10 \) K to \( T = 200 \) K under charge-transfer excitation and at room temperature the integrated intensity is \( \approx 25\% \) of the low temperature value. The absence of significant temperature quenching is attributed to the high energy position of the charge-transfer band which reduces nonradiative transitions within the [MnO₆]₃⁻ molecular complex.

The unactivated host lattice also exhibits Mn⁺⁺ emission due to the presence of this ion as contaminants (ppm range) in the TiO₆ starting material. In the excitation spectrum for Mn⁺⁺ emission the Gd³⁺ emission (φ → ²P transition at \( \approx 310 \) nm is also observed (Fig. 4). Since the Gd³⁺ emission overlaps with the Mn⁺⁺ charge-transfer band, the Mn⁺⁺ ions can act as efficient traps for the Gd³⁺ excitation energy. It is not possible to observe the Gd³⁺ line in the excitation spectrum of samples that are intentionally doped with Mn⁺⁺ ions due to the presence of the allowed ⁶S → Mn⁺⁺ charge-transfer band in the \( \approx 310 \) nm wavelength region.

The tetrahedral state of the Mn ions is the most stable oxidation state in this host lattice. Unlike the perovskites \( \text{(Sr, Ca)}_2\text{ZrO}_3 \) \( \text{5, 6} \) \( \text{(Sr, Ca)}\text{TiO}_3 \) \( \text{5, 6} \) and \( \text{LaAIO}_3 \)\( \text{6} \) where an oxygen anneal is necessary for Mn⁺⁺ stabilization, the synthesis of Mn-activated Gd₂MgTiO₆ in air stabilizes manganese ions in the tetrahedral state.

Conclusion

We have evaluated the optical properties of Mn⁺⁺ in Gd₂MgTiO₆, a distorted perovskite. The presence of multiple Mn⁺⁺ sites suggests a deviation from a perfect 1:1 order between the Mg²⁺ and Ti⁴⁺ on the B-site of this perovskite. The strong intensity of the main zero-phonon transition relative to its phonon side band indicates distortion of the TiO₆ octahedral groups where the Mn⁺⁺ substitutes. A crystal structure determination is needed to confirm these observations. In unactivated Gd₂MgTiO₆ we have observed Mn⁺⁺ emission due to its presence as contaminants in the TiO₆ starting material.

Electrochemical Evaluation of LaNi₅₋ₓGeₓ Metal Hydride Alloys

C. Witham,*a B. V. Ratnakumar,**b R. C. Bowman, Jr.,* A. Hightower,* and B. Fultz*

*Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, USA
**Electrochemical Technologies Group, Jet Propulsion Laboratory, Pasadena, California 91109, USA

ABSTRACT

We report a detailed evaluation of Ge-substituted LaNi₅ for electrochemical application as a negative electrode in alkaline rechargeable cells. Alloys with small substituents of Ge for Ni show operating pressures, chargeability, cyclic lifetime, and kinetics for hydrogen absorption and desorption all superior to those found in many other substituted LaNi₅ alloys. These improved properties were achieved with a minimal reduction in hydrogen storage capacity.

Introduction

One impediment to the widespread consumer use of LaNi₅ as a negative electrode in alkaline rechargeable batteries is its fast degradation of hydrogen absorption capacity experienced during charge-discharge cycling. An approach used to alleviate this degradation is to make substitutions of various metals for La as well as Ni. The partial substitution of solutes such as Ti, Zr, Nd, and Ce for La; and Co, Mn, Al, and Si for Ni have been shown to be successful for improving the cyclic lifetime. Another benefit of ternary solute substitution is the decrease in plateau pressure of the metal hydride, making it feasible to operate a nickel-metal hydride (Ni-MH) cell at low internal pressures. Sakai et al. performed a rigorous evaluation of several metals, M, as ternary solutes in LaNi₅₋ₓMₓ. The equilibrium hydriding pressure of the alloy decreased on substitution in the order Ni > (Cr, Co, Cu) > (Al, Mn), and the cyclic lifetime increased in the order Mn < Ni < Cu < Co < Al < Ce. In all these ternary alloys, however, the improvements in the cyclic lifetime and plateau pressure unfortunately are accompanied by a decrease in the hydrogen absorption capacity, long activation, or slow kinetics. The use of Sn as a partial substituent for Ni in LaNi₅ was found to reduce the plateau pressure and hysteresis, while retaining most of the absorption capacity of the binary alloy. Further, the Sn substituent was found to result in a 20-fold increase in the cyclic lifetime in gas-phase thermal cycling and a cyclic lifetime comparable to a multicomponent misch metal-based alloy in electrochemical charge-discharge cycling. The kinetics of electrochemical charge and discharge also became more facile on Sn substitution.

Encouraged by the improvement in the electrochemical performance of LaNi₅ on Sn substitution, we began studies of alloys prepared with other substituents from the main group of the periodic table. Germanium is one promising ternary substituent for Ni in LaNi₅ as suggested.

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alloys are single phase and have plateau pressures below 1 atm\textsuperscript{11} and our present experimental test cells are more amenable to the study of alloys of low (≤1 atm) absorption pressure.

**Experimental**

The LaNi\textsubscript{5−x}Ge\textsubscript{x} alloys were produced by induction-melting in an argon atmosphere and subsequent annealing in vacuum at 950°C for 72 h. Chemical composition analyses of the annealed alloys were performed with a JEOL Superprobe 733 electron microprobe. Phase fractions and unit cell lattice parameters were measured with an INEL CPS-120 powder diffractometer using Co K\textsubscript{α} radiation (\(\lambda = 1.7902\) Å). The gas-phase isotherms were obtained with an automated Sievert’s apparatus. The electrochemical measurements were performed on Teflon-bonded MH alloy disk electrodes (area = 0.09 cm\textsuperscript{2}), using an EG&G 273 potentiostat/galvanostat and a 1260 Solartron frequency-response analyzer integrated with an IBM-PC. The cycling of the prismatic electrodes (area = 6.45 cm\textsuperscript{2}) was performed in a negative-limited glass cell with NiOOH counterelectrodes and an Hg/HgO reference electrode, using an Arbin battery cycler. Details on the experimental equipment and sample preparation have been provided in our previous publication.\textsuperscript{8}

**Results and Discussion**

Figure 1 shows the x-ray diffraction (XRD) patterns of LaNi\textsubscript{5−x}Ge\textsubscript{x}, LaNi\textsubscript{4.6}Ge\textsubscript{0.4}, and the binary alloy. These diffraction patterns show that all materials are of single (Haucke) phase. There is an increase in the unit cell volume on substitution of Ge from a value of 86.8 Å\textsuperscript{3} for LaNi\textsubscript{5}, to 87.8 Å\textsuperscript{3} for LaNI\textsubscript{4.7}Ge\textsubscript{0.3} and 88.2 Å\textsuperscript{3} for LaNi\textsubscript{4.6}Ge\textsubscript{0.4}, as may be expected from substitution of Ni with an element having a larger metallic radius. Figure 2 shows three pres-
sure-composition-temperature (PCT) isotherms comparing the Ge-substituted alloys to the binary alloy at 25°C. As may be seen from these isotherms, the equilibrium pressure of 2 atm for binary LaNi₅ decreases to below 1 atm on Ge substitution at these compositions. This decrease in the equilibrium plateau pressure with increasing unit cell volume is consistent with the observations of Gruen et al.¹²

The gas-phase hydrogen absorption capacities of the Ge-substituted alloys are marginally lower than the binary alloy or the Sn-substituted alloys. The electrochemical capacities obtained with the Ge-substituted alloys are in the range of 250 to 300 mAh/g, and are comparable to that of Sn-substituted alloys or a multicomponent misch metal-based alloy of composition M₄Mn₃Co₀₇₅Mn₀₄Al₀₃ (Fig. 3). The high measured electrochemical capacity of the LaNi₅₉Ge alloys can be attributed in part to the reduced plateau pressure for hydrogen absorption. The binary alloy, which has a plateau pressure higher than 1 atm, is not charged effectively in our test cells, which maintain an internal pressure slightly above the ambient pressure.

The electrochemical kinetic parameters for the hydrogen absorption and desorption processes, measured by dc polarization (both linear and Tafel polarization) and ac impedance methods, are given in Table I. There is reasonable agreement among the values of the exchange current density (normalized by electrode geometric area) obtained from these three methods. The ternary substitution of Ge in LaNi₅ resulted in an increase in the exchange current density, as observed earlier with Sn.¹³ The improvement in the kinetics is almost comparable to a Sn-substituted alloy, LaNi₅₉Sn₀₂. In comparison to LaNi₅, the Ge-substituted alloys show improvement in all kinetic parameters except the Tafel slope on desorption. In addition, the kinetic parameters for the Ge-substituted alloys are generally better than those of LaNi₅₉Sn₀₂. In LaNi₅₉Sn alloys, the kinetics show a maximum at low compositions, x = 0.1 to 0.2, but increased Ge substitution seems to benefit the charge kinetics even at the higher compositions here.

Finally, the electrochemical capacity of the Ge-substituted alloys during charge-discharge cycling in negative-limited prismatic Ni-MH cells is shown in Fig. 4. The cells were charged over 5 h at 4.5 mA/cm² (60 mA/g) to 115% of charge return and discharged over 2 h at 12.5 mA/cm² (150 mA/g) to 0 V vs. Hg/HgO. The cyclic lifetime of the Ge-substituted alloys is compared with LaNi₅₉Sn₀₂₅ and a misch metal-based alloy evaluated earlier. The Ge-modified alloys have initial capacities slightly lower than those of the best Sn-substituted alloys, but similar to those with the same solute composition. Further, some Ge-modified alloys experience a quick loss of capacity in the first 30 cycles. This initial decline is not a function of the activation cycles and is being investigated. Despite this initial drop in capacity, the capacity retention of the Ge-modified alloys is excellent, especially in the latter stages of cycling. The rate of reduction in capacity after the initial fall is considerably less with the Ge-substituted alloys than in the Sn-substituted and misch metal-based MH alloys. Rates of capacity fade were 0.65 and 0.28 mAh/g/cycle for LaNi₅₉Ge₀₃ and LaNi₅₉Ge₀₄, 0.73 for LaNi₅₉Sn₀₂₅, and 0.72 for the misch metal-based MH alloys. The capacity of the

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Fig. 3. Capacities of (•) LaNi₅₉₉Ge and (■) LaNi₅₉Sn measured by (open symbols) gas-phase absorption to 5 atm and (closed symbols) prismatic cells. Horizontal line represents capacity of M₄Mn₃Co₀₇₅Mn₀₄Al₀₃ measured in prismatic cell.
LaNi$_x$Ge$_{y}$ alloy after the first 100 cycles exceeds that of any of the Sn-substituted alloys as well as the misch metal-based formulations.

**Conclusion**

The substitution of 6 and 8% of Ni with Ge in LaNi$_5$ improves its performance as an anode in alkaline rechargeable cells. The reduced absorption pressures facilitate the charging process and thus enhance the electrochemical capacity. Germanium substitution also leads to better absorption/desorption kinetics. More significantly, Ge substitution endows the material with excellent capacity retention during charge-discharge cycling. Overall, the effects of Ge substitution are similar to those of Sn, although the cyclic lifetime is superior. Detailed studies with the other Ge-based formulations are underway.

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