

its phonon side band. A distortion of the  $\text{TiO}_6$  octahedra (where the  $\text{Mn}^{4+}$  substitutes) in  $\text{Gd}_2\text{MgTiO}_6$  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  $\sim 95\%$  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  $[\text{MnO}_6]^{8-}$  molecular complex.

The unactivated host lattice also exhibits  $\text{Mn}^{4+}$  emission due to the presence of this ion as contaminants (ppm range) in the  $\text{TiO}_2$  starting material. In the excitation spectrum for  $\text{Mn}^{4+}$  emission the  $\text{Gd}^{3+} {}^8\text{S} \rightarrow {}^6\text{P}$  transition at  $\sim 310$  nm is also observed (Fig. 4). Since the  $\text{Gd}^{3+}$  emission overlaps with the  $\text{Mn}^{4+}$  charge-transfer band, the  $\text{Mn}^{4+}$  ions can act as efficient traps for the  $\text{Gd}^{3+}$  excitation energy. It is not possible to observe the  $\text{Gd}^{3+}$  line in the excitation spectrum of samples that are intentionally doped with  $\text{Mn}^{4+}$  ions due to the presence of the allowed  $\text{O}^{2-}$  to  $\text{Mn}^{4+}$  charge-transfer band in the  $\sim 310$  nm wavelength region.

The tetravalent state of the Mn ions is the most stable oxidation state in this host lattice. Unlike the perovskites ( $\text{Sr}$ ,  $\text{Ca}$ ) $\text{ZrO}_3$ ,<sup>6,15</sup> ( $\text{Sr}$ ,  $\text{Ca}$ ) $\text{TiO}_3$ ,<sup>15</sup> and  $\text{LaAlO}_3$ ,<sup>6</sup> where an oxygen anneal is necessary for  $\text{Mn}^{4+}$  stabilization, the synthesis of Mn-activated  $\text{Gd}_2\text{MgTiO}_6$  in air stabilizes manganese ions in the tetravalent state.

### Conclusion

We have evaluated the optical properties of  $\text{Mn}^{4+}$  in  $\text{Gd}_2\text{MgTiO}_6$ , a distorted perovskite. The presence of multiple  $\text{Mn}^{4+}$  sites suggests a deviation from a perfect 1:1 order between the  $\text{Mg}^{2+}$  and  $\text{Ti}^{4+}$  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  $\text{TiO}_6$  octahedral groups where the  $\text{Mn}^{4+}$  substitutes. A crystal structure determination is needed to confirm these observations. In unactivated  $\text{Gd}_2\text{MgTiO}_6$  we have observed  $\text{Mn}^{4+}$  emission due to its presence as contaminants in the  $\text{TiO}_2$  starting material.

## Electrochemical Evaluation of $\text{LaNi}_{5-x}\text{Ge}_x$ Metal Hydride Alloys

C. Witham,<sup>\*a</sup> B. V. Ratnakumar,<sup>\*\*b</sup> R. C. Bowman, Jr.,<sup>a</sup> A. Hightower,<sup>a</sup> and B. Fultz<sup>a</sup>

<sup>a</sup>Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, USA

<sup>b</sup>Electrochemical Technologies Group, Jet Propulsion Laboratory, Pasadena, California 91109, USA

### ABSTRACT

We report a detailed evaluation of Ge-substituted  $\text{LaNi}_5$  for electrochemical application as a negative electrode in alkaline rechargeable cells. Alloys with small substitutions 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  $\text{LaNi}_5$  alloys. These improved properties were achieved with a minimal reduction in hydrogen storage capacity.

### Introduction

One impediment to the widespread consumer use of  $\text{LaNi}_5$  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.<sup>1,2</sup> 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.*<sup>3</sup> performed a rigorous evaluation of several metals, M, as ternary solutes in  $\text{LaNi}_{5-x}\text{M}_x$ . The equilibrium hydriding pressure of the alloy decreased on substitution in the order  $\text{Ni} > (\text{Cr}, \text{Co}, \text{Cu}) > (\text{Al}, \text{Mn})$ , and the cyclic lifetime increased in the order  $\text{Mn} < \text{Ni} < \text{Cu} < \text{Cr} < \text{Al} < \text{Co}$ . In all these ternary alloys, however, the

Manuscript submitted May 3, 1996; revised manuscript received June 25, 1996.

General Electric assisted in meeting the publication costs of this article.

### REFERENCES

1. K. H. Butler, *Fluorescent Lamp Phosphors*, Pennsylvania State University Press, University Park, PA (1980).
2. A. M. Srivastava and T. F. Soules, *Luminescent Materials (Phosphors)*, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. 15, John Wiley & Sons, New York (1995).
3. M. German and L. M. Kovbe, *Russian J. Inorg. Chem.*, **28**, 586 (1983).
4. A. M. Srivastava and W. W. Beers, To be published.
5. G. Blasse and P. H. M. De Korte, *J. Inorg. Nucl. Chem.*, **43**, 1505 (1981).
6. M. E. van Ipenburg, G. J. Dirksen, and G. Blasse, *Mater. Chem. Phys.*, **39**, 236 (1995).
7. A. M. Srivastava and J. F. Ackerman, *Chem. Mater.*, **4**, 1011 (1992); A. M. Srivastava and J. F. Ackerman, *J. Solid State Chem.*, **98**, 144 (1992); A. M. Srivastava and J. F. Ackerman, *Mater. Res. Bull.*, **26**, 443 (1991).
8. G. Blasse, *J. Chem. Phys.*, **48**, 3108 (1968); G. Blasse and A. Brill, *ibid.*, **57**, 187 (1968); G. Blasse and G. J. Dirksen, *Inorg. Chim. Acta.*, **157**, 141 (1989).
9. G. Blasse and A. F. Cormit, *J. Solid State Chem.*, **6**, 513 (1973).
10. J. T. Last, *Phys. Rev.*, **105**, 1740 (1957).
11. S. Geshwind *ibid.*, **126**, 1685 (1962).
12. J. E. Donegan, T. J. Glynn, G. F. Imbusch, and J. P. Rameika, *J. Lumin.*, **36**, 93 (1986).
13. M. R. Lorenz and J. J. Prener, *J. Chem. Phys.*, **25**, 1013 (1956).
14. A. Brenier, A. Suchocki, C. Pedrini, G. Boulon, and C. Madej, *Phys. Rev.*, **B46**, 3219 (1992).
15. G. Blasse, P. H. M. De Korte, and A. Mackor, *J. Inorg. Nucl. Chem.*, **43**, 1499 (1981).

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  $\text{LaNi}_5$  was found to reduce the plateau pressure and hysteresis, while retaining most of the absorption capacity of the binary alloy.<sup>4</sup> Further, the Sn substituent was found to result in a 20-fold increase in the cyclic lifetime in gas-phase thermal cycling<sup>5</sup> and a cyclic lifetime comparable to a multicomponent misch metal-based alloy in electrochemical charge-discharge cycling.<sup>6,8</sup> The kinetics of electrochemical charge and discharge also became more facile on Sn substitution.<sup>8</sup>

Encouraged by the improvement in the electrochemical performance of  $\text{LaNi}_5$  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 solute thus identified. From gas-phase studies,<sup>9,10</sup> Ge substitution has been reported earlier to reduce the absorption pressures of  $\text{LaNi}_5$ . We report here the behavior of Ge-substituted  $\text{LaNi}_5$  alloys as negative electrodes in alkaline electrolytes for Ni-MH cells. Solute compositions of  $x = 0.3$  and 0.4 in  $\text{LaNi}_{5-x}\text{Ge}_x$  were chosen for this study because these

\* Electrochemical Society Student Member.

\*\* Electrochemical Society Active Member.

alloys are single phase and have plateau pressures below 1 atm,<sup>9,11</sup> and our present experimental test cells are more amenable to the study of alloys of low ( $\leq 1$  atm) absorption pressure.

### Experimental

The  $\text{LaNi}_{5-x}\text{Ge}_x$  alloys were produced by induction-melting in an argon atmosphere and subsequent annealing in vacuum at  $950^\circ\text{C}$  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  $\text{Co K}_\alpha$  radiation ( $\lambda = 1.7902 \text{ \AA}$ ). 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 =  $0.09 \text{ cm}^2$ ), 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 =  $6.45 \text{ cm}^2$ ) was performed in a negative-limited glass cell with  $\text{NiOOH}$  counterelectrodes and an  $\text{Hg/HgO}$  reference electrode, using an Arbin battery cycler. Details on the experimental equipment and sample preparation have been provided in our previous publication.<sup>8</sup>

### Results and Discussion

Figure 1 shows the x-ray diffraction (XRD) patterns of  $\text{LaNi}_{4.7}\text{Ge}_{0.3}$ ,  $\text{LaNi}_{4.6}\text{Ge}_{0.4}$ , 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  $86.8 \text{ \AA}^3$  for  $\text{LaNi}_5$ , to  $87.8 \text{ \AA}^3$  for  $\text{LaNi}_{4.7}\text{Ge}_{0.3}$  and  $88.2 \text{ \AA}^3$  for  $\text{LaNi}_{4.6}\text{Ge}_{0.4}$ , as may be expected from substitution of Ni with an element having a larger metallic radius. Figure 2 shows three pres-

Fig. 1. XRD patterns of  $\text{LaNi}_{4.6}\text{Ge}_{0.4}$ ,  $\text{LaNi}_{4.7}\text{Ge}_{0.3}$ , and  $\text{LaNi}_5$ . Powders were activated with four gas-phase hydrogen absorption-desorption cycles before measurement.

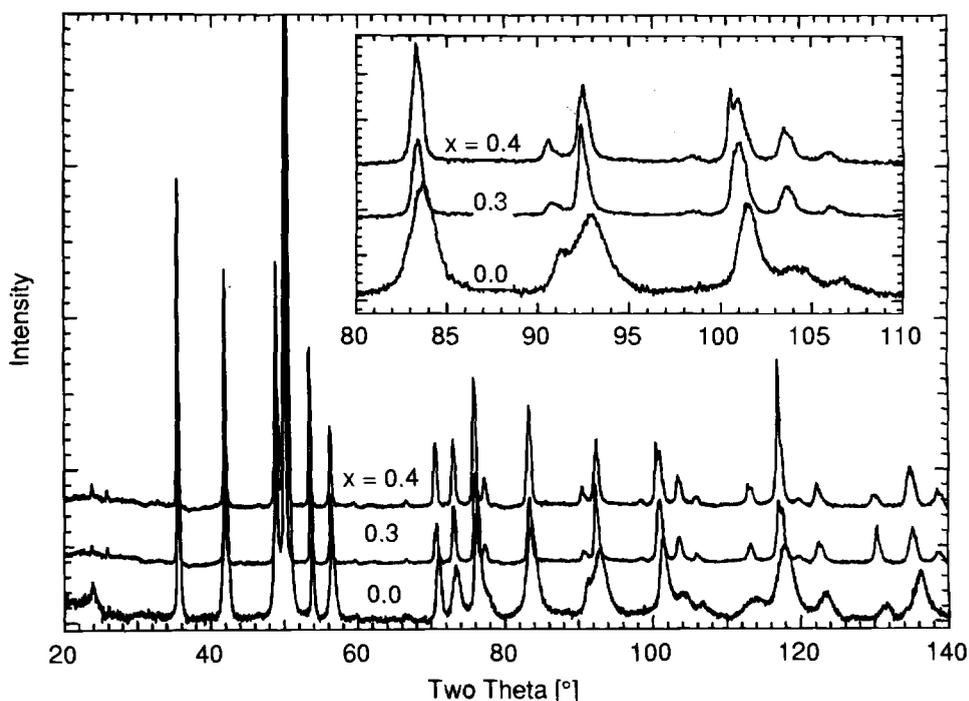
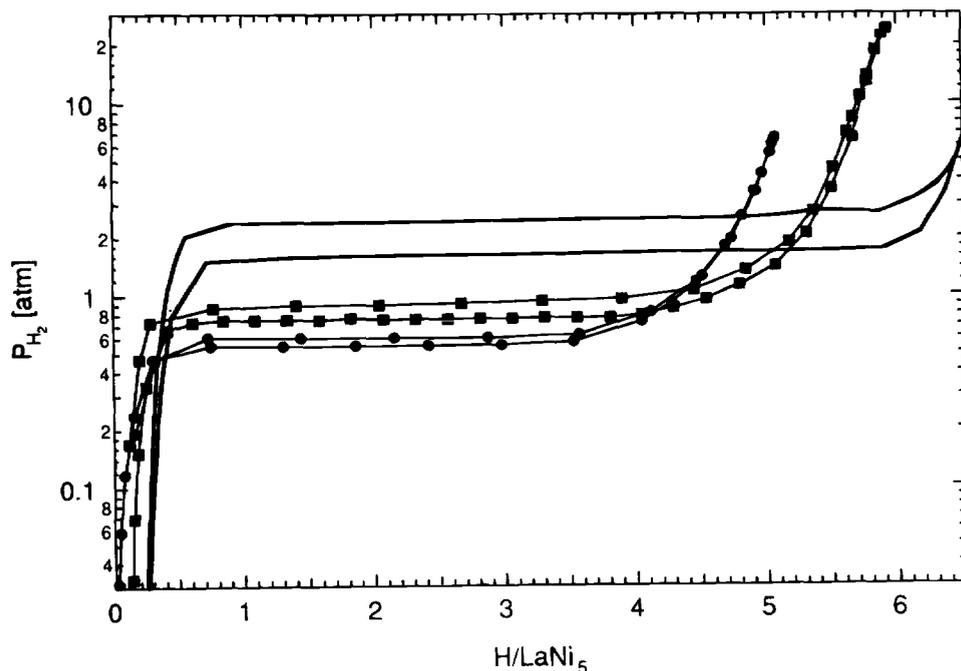


Fig. 2. Gas-phase PCT isotherms of (—)  $\text{LaNi}_5$ , (■)  $\text{LaNi}_{4.7}\text{Ge}_{0.3}$ , and (●)  $\text{LaNi}_{4.6}\text{Ge}_{0.4}$  measured at  $23^\circ\text{C}$ .



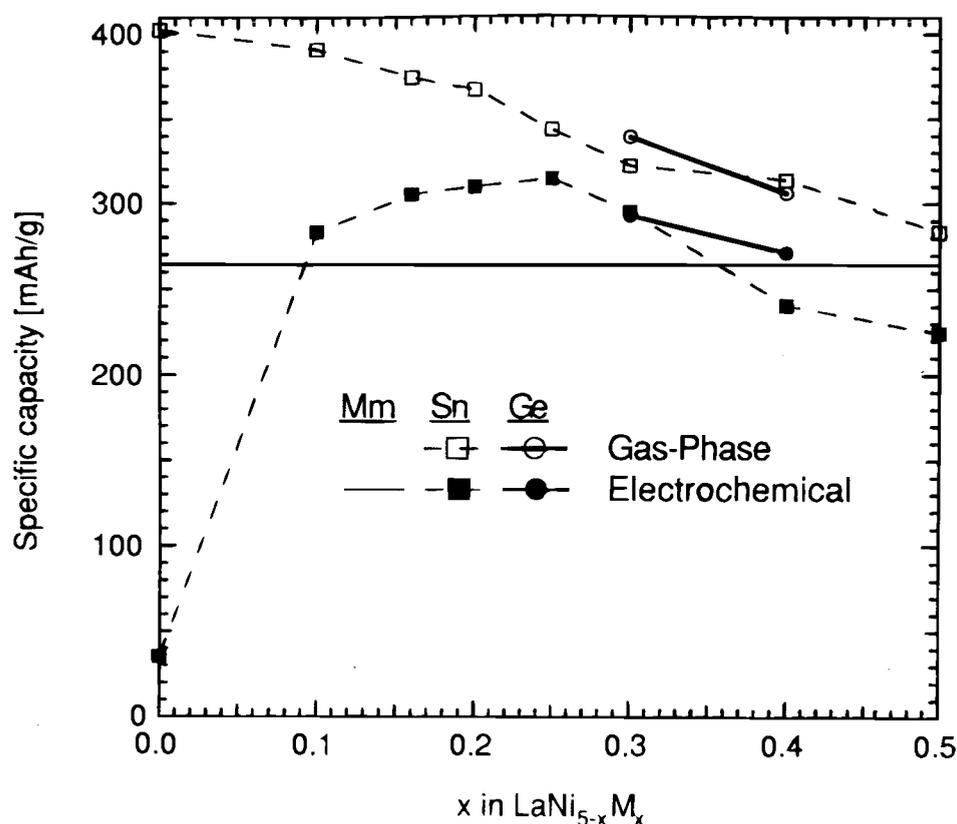


Fig. 3. Capacities of (●) LaNi<sub>5-x</sub>Ge<sub>x</sub> and (■) LaNi<sub>5-x</sub>Sn<sub>x</sub> measured by (open symbols) gas-phase absorption to 5 atm and (closed symbols) prismatic cells. Horizontal line represents capacity of MmNi<sub>3.68</sub>Co<sub>0.75</sub>Mn<sub>0.4</sub>Al<sub>0.3</sub> measured in prismatic cell.

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 LaNi<sub>5</sub> 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.*<sup>12</sup>

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 MmNi<sub>3.68</sub>Co<sub>0.75</sub>Mn<sub>0.4</sub>Al<sub>0.3</sub> (Fig. 3). The high measured electrochemical capacity of the LaNi<sub>5-x</sub>Ge<sub>x</sub> 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 LaNi<sub>5</sub> resulted in an increase in the exchange current density, as observed earlier with Sn.<sup>8</sup> The improvement in the

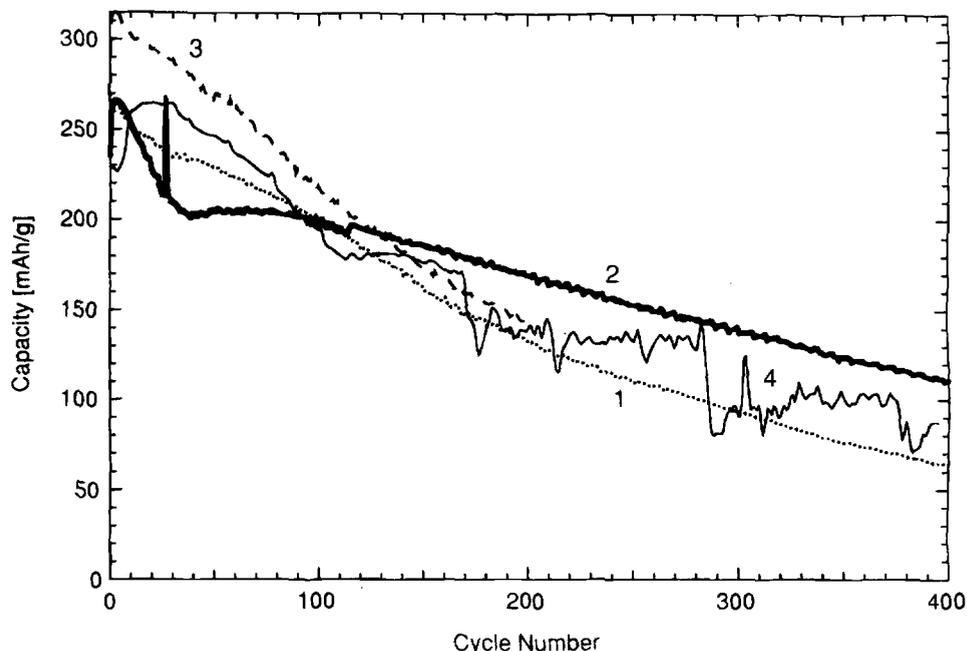
kinetics is almost comparable to a Sn-substituted alloy, LaNi<sub>4.8</sub>Sn<sub>0.2</sub>. In comparison to LaNi<sub>5</sub>, the Ge-substituted alloys show improvement in all kinetic parameters except the Tafel slope on desorption. In addition, the kinetic parameters for the Ge-substituted alloys are generally better than those of LaNi<sub>4.8</sub>Sn<sub>0.2</sub>. In LaNi<sub>5-x</sub>Sn<sub>x</sub> alloys, the kinetics show a maximum at low compositions, x = 0.1 or 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/cm<sup>2</sup> (60 mA/g) to 115% of charge return and discharged over 2 h at 12.5 mA/cm<sup>2</sup> (150 mA/g) to -0.5 V vs. Hg/HgO. The cyclic lifetime of the Ge-substituted alloys is compared with LaNi<sub>4.75</sub>Sn<sub>0.25</sub> 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 LaNi<sub>4.7</sub>Ge<sub>0.3</sub> and LaNi<sub>4.6</sub>Ge<sub>0.4</sub>, 0.73 for LaNi<sub>4.75</sub>Sn<sub>0.25</sub>, and 0.72 for the misch metal-based MH alloys. The capacity of the

Table I. Kinetic parameters of LaNi<sub>5-x</sub>M<sub>x</sub> alloys in 5.5 M KOH solution.

Alloy	Micro-polarization <i>i</i> <sub>0</sub> (mA/cm <sup>2</sup> )	Tafel polarization		AC impedance <i>i</i> <sub>0</sub> (mA/cm <sup>2</sup> )	
		<i>i</i> <sub>0</sub> (mA/cm <sup>2</sup> )	Absorption Slope (mV/decade)		Desorption Slope (mV/decade)
LaNi <sub>5</sub>	8.6	10.7	242	108	11.3
LaNi <sub>4.8</sub> Sn <sub>0.2</sub>	11.3	32.7	185	220	12.8
LaNi <sub>4.7</sub> Ge <sub>0.3</sub>	12.0	38.3	195	182	12.9
LaNi <sub>4.6</sub> Ge <sub>0.4</sub>	12.7	31.7	217	184	13.4

Fig. 4. Cyclic lifetimes of negative-limited Ni-MH cells; (1) (---)  $\text{LaNi}_{4.7}\text{Ge}_{0.3}$ , (2) (—)  $\text{LaNi}_{4.6}\text{Ge}_{0.4}$ , (3) (---)  $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ , and (4) (—)  $\text{Mm}(\text{NiCoMnAl})_5$ .



$\text{LaNi}_{4.6}\text{Ge}_{0.4}$  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  $\text{LaNi}_5$  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.

### Acknowledgment

This work was carried out at the Jet Propulsion Laboratory under contract with the National Aeronautics and Space Administration and at the California Institute of Technology under funding by DOE Grant DE-FG03-94ER14493. We thank NASA for providing the facilities for the electrochemical studies and DOE for support for all the authors and the Sievert's apparatus at Caltech.

Manuscript submitted May 16, 1996; revised manuscript received July 1, 1996.

Jet Propulsion Laboratory assisted in meeting the publication costs of this article.

### REFERENCES

1. T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, and K. Oguru, *J. Less-Common Met.*, **159**, 127 (1990); T. Sakai, M. Matsuoka, and C. Iwakura, in *Handbook on the Physics and Chemistry of Rare Earths*, K. A. Gschneidner, Jr. and L. Eyring, Editors, Vol. 21, Elsevier Science B. V., Amsterdam (1995).
2. G. D. Adzic, J. R. Johnson, J. J. Reilly, J. McBreen, S. Mukerjee, M. P. S. Kumar, W. Zhang, and S. Srinivasan, *This Journal*, **142**, 3429 (1995).
3. T. Sakai, K. Oguru, H. Miyamura, N. Kuriyama, A. Kato, and H. Ishikawa, *J. Less-Common Met.*, **161**, 193 (1990).
4. S. Luo, W. Luo, J. D. Clewley, T. B. Flanagan, and L. A. Wade, *J. Alloys Compounds*, **231**, 467 (1995).
5. R. C. Bowman, Jr., C. H. Luo, C. C. Ahn, C. K. Witham, and B. Fultz, *ibid.*, **217**, 185 (1995).
6. B. V. Ratnakumar, G. Halpert, C. Witham, and B. Fultz, *This Journal*, **141**, L89 (1994).
7. B. V. Ratnakumar, S. Surampudi, S. Di Stefano, G. Halpert, C. Witham, A. Hightower, and B. Fultz, in *Hydrogen and Metal Hydride Batteries*, P. D. Bennett and T. Sakai, Editors, PV 94-27, p. 57, The Electrochemical Society Proceedings Series, Pennington, NJ (1994).
8. B. V. Ratnakumar, C. Witham, R. C. Bowman, Jr., A. Hightower, and B. Fultz, *This Journal*, **143**, 2578 (1996).
9. M. H. Mendelsohn, D. M. Gruen, and A. E. Dwight, *Mater. Res. Bull.*, **13**, 1221 (1978).
10. M. Mendelsohn, D. Gruen, and A. Dwight, *Inorg. Chem.*, **18**, 3343 (1979).
11. C. Witham, R. C. Bowman, Jr., and B. Fultz, *J. Alloys Compounds*, Submitted.
12. M. H. Mendelsohn, D. M. Gruen, and A. E. Dwight, *J. Less-Common Met.*, **63**, 193 (1979).