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# Hydrogen-accumulating Materials in Electrochemical Systems

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**Abstract** — Intermetallic compounds capable of absorbing large amounts of hydrogen attract attention due to their applied significance in the production of chemical power sources. A variety of such compounds have been studied. The present paper gives some examples of hydrogen-absorbing intermetallides and describes their preparation, as well as touches upon some problems of hydride-forming alloys. The survey covers results obtained over the past decade.
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The development of electrochemical devices employing hydrogen as an active material for electric power generation dates back to the eve of electrochemistry, since Grove's experiment [1] in 1839 can be considered as a realization of a prototype of contemporary hydrogen–oxygen fuel cells. At present three principal types of electrochemical systems are recognized: (1) fuel cells with hydrogen and oxygen (air) delivered to the anode and cathode, respectively; (2) systems with a gaseous hydrogen on the anode and a solid cathode used in traditional accumulators (semi-gas accumulators or semi-fuel cells); and (3) rechargeable systems that accumulate hydrogen on charging.

The best known system of the second type is a nickel–hydrogen accumulator developed in 1964 at State Research Design and Construction and Technological Accumulator Institute (Soviet Union) [2]. The hydrogen electrode in this accumulator was made of a thin porous metal–ceramic nickel support with microquantities of platinum applied from a chloroplatinic acid solution by means of the cementation process. The cathode was nickel oxide.

Third-type systems have become actively developed in 1960s after the discovery of the ability of certain intermetallic compounds (IMCs) to reversibly absorb considerable quantities of hydrogen, up to 1.5–7 wt%, at moderate pressures and temperatures. The first accumulator with $LaNi_5$ as a base for a metal hydride electrode and a nickel oxide electrode has been patented in 1975. The commercial epoch of nickel–metal hydride (NiMH) power sources dates back to 1990s, and since then the production of such sources has mounted up. According to [3], from 1995 to 2003 the yearly production of NiMH accumulators has increased from 310 to 1950 million units against 1590 to 2010 million units for traditional Ni–Cd accumulators.

The competitiveness and perspectiveness of nickel–metal hydride accumulators are primarily due to the high-density of stored energy, ecological safety, and interchangeability, in view of the closeness in principal characteristics, with nickel–cadmium batteries. At present NiMH accumulators are widely applied in cell phones, portable computers, video- and phototechnique, medical equipment, and illumunation and burglar and fire alarm systems, i.e. devices whose market is constantly expanding. Motor industry, too, shows great interest in these systems.

The production of NiMH accumulators is rapidly growing, but simultaneously research into their improvement on the basis of new hydrogen-absorbing materials is being in progress. This makes advances in this quite difficult to summarize, since reviews and monographs [4–6] become out of date fairly rapidly. This concise review presents certain topical problems of research and application of hydride-forming materials. It should be emphasized that the term "hydride-forming," which is commonly used in the literature, is arbitrary, since the question of what is the actual state of hydrogen in materials is still open. Most emphasis in this review is put on recent works that have not been covered in the above-mentioned reviews and monographs, as well as on works that have not been given due attention.

## PRINCIPLE OF OPERATION OF NIMH SYSTEMS AND REQUIREMENTS FOR HYDRIDE-FORMING SYSTEMS

Discharge of the positive electrode of an NiMH system results in the reduction of nickel(III) hydroxide to nickel(II) hydroxide, whereas when the electrode is charged from an external power source, the reverse process takes place:

$$NiOOH + H_2O + \bar{e} \longrightarrow Ni(OH)_2 + OH^-.$$

On the negative electrode, discharge produces ionization of the hydride hydrogen and charge, hydride formation:

$$MH_x + xOH^- \longrightarrow M + xH_2O + x\bar{e}.$$

Thus, the overall operating scheme can be represented as follows:

$$MH + NiOOH \longrightarrow M + Ni(OH)_2.$$

The emf of such a power source is about 1.3 V (nominally, ~1.12 V).

A hydride-forming material should possess the following properties: high hydrogen sorption capacity; fast initiation of the hydride electrode; low self-discharge rate; resistance to corrosion: and mechanical stability. A hydrogen-accumulating material should have as wide working temperature range as possible and the equilibrium hydride formation pressure meeting working conditions; withstand multiple charge–discharge cycles, be capable of charging and discharging at high current densities; be resistant to redischarge and recharge. Low cost and environmental safety are also of importance. Safe behavior of the material and system as a whole in certain emergency situations, say on short circuit.

## EXAMPLE HYDROGEN-ACCUMULATING SYSTEMS

At present a huge number of hydrogen-absorbing materials have been described. Forty eight metals are known to be basically capable of absorbing hydrogen. A very high gravimetric capacity is characteristic of magnesium: 2200 mA h $g^{-1}$ at a hydrogen density of 7.6 wt%. However, the high hydrogen desorption temperature, and low dissociation pressure and extremely low desorption rate of hydrides prevent the potential of this system for electrochemical devices from being employed. The above requirements are primarily met by Ti, Zr, or rare-earth metal alloys, and the permanent component of such alloys is, as a rule, nickel. The tested alloys include $AB_5$, $AB_2$, AB, $A_2B$, $AB_3$, $A_2B_7$, $A_2B_{17}$, and $AB_2C_9$, and the best results were obtained with AB5, AB2, AB, and AB2+AB. The symbols A, B, and C relate to several elements; the crystal chemical site of substitution is also taken into account. Practically applied materials are multicomponent multiphase and/or composite systems. The search for materials is largely empirical. The richest, in terms of the number of components, alloy on record contains nine elements: V, Ti, Zr, Ni, Cr, Co, Mn, Al, and Sn (hydrogen capacity 440 mA h $g^{-1}$). Particular emphasis is placed on amorphous, film, and nanocrystalline materials [7]. In certain systems, amorphous materials have a lower capacity but better dynamic discharge–charge characteristics.

The highest theoretical capacities are characteristic of $Mg_2Ni$ (999 mA h $g^{-1}$) and $ZrV_2$ (763 mA h $g^{-1}$), but in practice such parameters have never been attained in electrochemical devices. Moreover, Mg–Ni systems are almost impractical because of corrosion sensitivity of magnesium and, as a consequence, high self-discharge. However, good discharge characteristics and relatively low cost still attract attention to magnesium-containing materials [8–10], whereas doping with, for example, Ti or Sc, allows satisfactory capacities and even cycling to be attained [11]. The intermetallide $LaNi_5$ has a fairly moderate theoretic capacity (375 mA h $g^{-1}$), but it is materials on the basis of this intermetallide with La and Ni partially replaced by other elements have enjoyed the widest practical application. Instead of pure rareearth metals, commercial electrodes are fabricated of their cheaper mixture, so-called mishmetal (commonly designated as μm or Ml, depending on whether cerium or lanthanum, respectively, prevails in the mixture). The average composition of one of the most widespread commercial alloys has the formula $MmNi_{3.55–3.6}\cdot Co_{0.7–0.75}Mn_{0.3–0.4}Al_{0.3–0.4}$, and its standard discharge capacity is 260–270 mA h $g^{-1}$. Intermetallic compounds like $AB_2$, too, have found application (the most known alloy of this type was given the name Ovonic by the initial letters of the name of its inventor Ovshinsky [12]). Active research on such systems containing Zr, Ti, Mn, V, Ni, and Cr is being continued [13–20]. The alloy $V_4Nb_{0.047}Ta_{0.047}TiNi_{0.56}\cdot Co_{0.14}$ is one of the best examples of this type systems.

The potential–current curves obtained on the direct current discharge of a hydrogen-saturated electrode contain plateaus corresponding to phase transitions. The plateau length relates to the quantity of hydrogen accumulated in the hydride, and the potential, to the effective pressure of hydride formation. With multiphase alloys, two or more discharge–charge plateaus are observed [21]. The two-plateau absorption iso-

therms of certain $AB_3$ and $A_2B_7$, observed in gas-phase experiments, [22, 23], have never been observed in electrochemical experiments. This is most likely related to the technology of fabrication of metal hydride electrodes. Note that such curves were obtained for certain materials with intercalated alkali metals [24]. Thus, research into discharge–charge regularities of hydride-forming materials is of general importance for various power sources.

Recently carbon nanostructures have come into use as hydride-forming materials. Electrodes of fullerenes [25, 26], single- and multiwall carbon nanotubes [27–29], charcoals [30], soot [31] etc. have been tested. However, no unambiguous evidence showing that carbon materials hold much promise has obtained, primarily because of data divergence. The possible reason for such a divergence is the contamination of carbon nanomaterials with metals which are capable of catalyzing hydrogen sorption processes. Furthermore, carbon surfaces are known to contain various redox groups that can under conversions in charge–discharge cycles, and the number and nature of these groups depend on the prehistory of the material. Combined materials of IMCs, for example, Mg–Ni systems, and carbon nanotubes hold certain promise [32].

Attempted prediction of the sorption capacity of alloys and optimization of new efficient hydrogenaccumulating systems are based on the consideration of thermodynamic, structural, and electronic factors, as well as composition–structure correlations. Jaksic [33] made use of the theory, according two which electrochemical sorption of hydrogen should be characteristic of alloys of transition metals having vacant *d* orbitals (hypo-d-electron metals, such Ti, Zr, Y, Sc, Hf, Mo, and W) with transition metals having innershell paired d electrons (hyper-d-electron metals, such as Ni, Fe, Co). On such material surfaces, highly electrocatalytically active hypo–hyper-*d*-electron metal combinations can arise. Ezaki et al. [34] invoked the above reasoning to explain the behavior of transition metals and alloys on cathodic generation of hydrogen [34].

Over the past years growing interest has been attached to quantum-chemical computations of hydrogen sorption by different materials [35–37]. At the same time, it is necessary to bear in mind that a material should combine not only the high hydrogen capacity of alloys and their electrocatalytic properties, but also many other important characteristics mentioned above.

Concentrated aqueous KOH and NaOH with various additives are used as electrolytes in NiMH accumulators. Thus, LiOH is added for low-temperature operation. The crystal hydrate $(CH_3)_4NOH \cdot 5H_2O$, as well as such solid electrolytes as polymeric gels, $Sb_2O_5 \cdot xH_2O$, and others were also suggested [38, 39]. Instead of nickel oxide, manganese dioxide can also serve as the positive electrode [38]. Systems with a metal hydride anode, a lead dioxide cathode, and a sulfuric acid electrolyte are known. Attempted use for the electrolyte of phosphoric acid doped with silica was reported [40].

## FABRICATION OF HYDROGEN-ACCUMULATING MATERIALS AND ELECTRODES THEREOF

The electrochemical properties of hydrogen-accumulating electrodes are largely determined by their fabrication method, and, therefore, this problem receives primary emphasis. Classical methods are based on alloying of a mixture of components, followed by long-term exposure of the alloy to high temperatures in a vacuum for homogenization. Powder metallurgy sometimes provides good results, especially in cases when the melting points of the components are quite different.

Mechanic alloying in ball mills has come into a fairly wide use. This method is advantageous in that it allows preparation of highly active superfine powders. This method, too, is suitable for fabrication of compositions whose components radically differ from each other in melting points [41]. Therewith, various dopants, such as carbon or graphite, are used fairly frequently [42]. Metal (Cu, Ni, Co, Fe, Zn, Cd) coating is also possible [5].

The gas atomizing method [43] allows fabrication of materials with enhanced cyclic stability. Moreover, with certain IMCs, fine particles (<20 μm) suffering no further crushing on operation could be obtained. Fairly good electrodes are produced by vacuum vapor deposition of composite materials on conducting supports [44].

Self-propagating high-temperature synthesis (Merzhanov's process) [45] and reduction of a mixture of oxides and salts with lithium hydride [46] have been applied.

Quite important is to develop appropriate procedures for activation and modification of alloy surfaces (treatment with alkali, hydrofluoric acid, hydrazine, or boron hydrides, polarization, microencapsulation, etc.). Scanning tunnel microscopy (STM), Raman spectroscopy, and other techniques make it possible to observe segregation phenomena in the surface layer [47]. Microencapsulation by electroless copper deposition

imparts corrosion resistance to electrodes and improves some other their properties [48]. Activation conditions are especially important for $AB_2$ materials which are readily coated with stable titanium and/or zirconium oxides. Some schemes for activation of such alloys in an alkali solution under reflux have been proposed [49]. The effect of fluorination and mixing of $AB_2$ and $AB_5$ alloys on their behavior [50], as well as the positive effect of μm dopants on $AB_2$ alloys have been demonstrated [51]. It is to be noted that etching activation affects strongly the chemical composition of the surface layer, since components dissolve at different rates.

Potentiostatic and galvanostatic pulse techniques have also been proposed for activation of $AB_2$ alloys [52].

In fabrication of metal hydride electrodes main emphasis is put on prevention of active mass losses due to cracking on saturation with hydrogen and provision for high conductivity and complete utilization of the material in charge–discharge cycles. Of key importance are binders which impart shape-preserving properties to the electrodes. Polymeric and metallic binders or their combinations are used; the compositions also include hydrophilizing agents. Copper powder is frequently used due to its high conductivity and good mechanic properties. Binder not only plays a shape-forming role, but also is somehow involved in charge–discharge processes [53]. Carriers for hydrogen-accumulating materials are also of importance. Successful use of nickel foams for this purpose has been reported [54]. With certain alloys, fast quenching makes for greater number of chargeδischarge cycles [55].

There has been some information that magnetic treatment affects the electrochemical properties of the $La_{0.9}Sm_{0.1}Ni_{2.0}Co_{3.0}$ alloy [56].

## OTHER SYSTEMS WITH HYDROGEN-ACCUMULATING ELECTRODES

Of certain interest are other systems with hydrogen-accumulating electrodes, related to those described above. As far back as 1980, a combination of a metal hydride and air electrodes had been suggested [57]. Chartouni et al. [58] used a metal hydride anode and a bifunctional air electrode with an $La_{0.6}Ca_{0.4}CoO_3$ perovskite catalyst. With gaseous hydrogen delivered on the anode, a fuel cell with a metal hydride anode can be obtained. For developing such systems, knowledge of the regularities of ionization of molecular hydrogen on metal hydride materials is necessary.

Hydrogen-containing compounds, such as hydrazine, hypophosphites, and boron hydrides, whose alkaline solutions are sufficiently stable, have fairly recently been suggested for saturation of metal electrodes with hydrogen and its subsequent oxidation with current generation [59]. Over the past decades [60–63] there has been a rebirth of interest in such systems, since they allow creation of power sources with higher emf. Thus, the emf of the system based on sodium boron hydride is 1.64 V. Devices with sodium boron hydride as a fuel and hydrogen peroxide as an oxidant have been developed [64].

## CERTAIN PROBLEMS OF THE ELECTROCHEMISTRY OF HYDROGEN-ACCUMULATING MATERIALS

There is no doubt that hydrogen will become one of the main energy sources in future and that hydrogen-accumulation materials holds much promise for hydrogen power industry and meets, first of all, safety requirements. However, the characteristics of present-day metal hydride batteries, especially of those of low-capacity (below 1.3 wt% hydrogen) materials, are still not good enough for future applications. Search for materials with higher discharge capacities is a topical problem. In particular, much attention now focuses on Mg-containing composites [65–67]. Research on modification of IMCs with platinum metal dopants [68], which improves many properties of alloys, but is open to cost rise, is in progress. Reduction of self-discharge, too, is a major focus of attention [69]. Fine phase transitions attendant in charge and discharge call for detailed study [70].

A number of other topical problems of this area of electrochemical materials science can be mentioned. Thus, a large group of problems is associated with correlation of the capacity of alloys for hydrogen sorption with the nature of their components. The role of structural and dimensional (size-related) factors in this phenomenon, as well as nonstoichiometry of IMC and phase segregation is yet to be found out.

Equally serious is the problem of hydrogen transport in IMC, in particular, quite an interesting diffusion phenomenon [71–74], when voltages produced by saturation with hydrogen force hydrogen atoms to move against their concentration gradient (non-Fickian diffusion). To solve these problems, appropriate model systems should be chosen. This is a very difficult task, since single-crystal samples are required. Apparently, some questions can be answered using the examples of palladium and some its alloys [75]. However, these systems by no means exhaust the entire diversity of diffusion phenomena in hydrides.

Hydrogen diffusion is studied both by electrochemical and various physical methods [76, 77].

A lot of questions are raised by the kinetics of hydrogen liberation from and ionization on hydrogen-accumulating materials. Up to now there has been little systematic work on the corrosion behavior of such materials [78, 79], which can be controlled by various additives both in the electrolyte solution [80] and in the electrode material [81]. To extend the working temperature range of hydrogen-accumulating electrodes is of importance [82, 83].

The first publication on the simulation of hydrogen-accumulating electrodes as systems with double distribution parameters appeared in Russia [84]. Later several research groups reported results in this field. This line of research is still urgent, and simulation of hydrogen-accumulating systems in different working conditions is important for optimizing devices and materials [85–91].

The information on metal hydride batteries of optimized design has appeared [92]. The diversity of electrocatalytic properties allows these systems to be employed in some other devices, specifically reactors for electrocatalytic hydrogenation and sensors.

The growing production of metal hydride batteries has already generated a demand for searching for ways of utilization of spent NiMH batteries [93].

## REFERENCES


1. Grove, W.R., *Philos. Mag.,* 1839, vol. 14, p. 127.
2. USSR Inventor's Certificate no. 194155, *Byull. Izobret.,* 1968, no. 23.
3. Lipp, L. and An, W., *J. Electrochem. Soc.,* 2005, vol. 152, no. 12, p. K1.
4. Petrii, O.A., Vasina, S.Ya., and Korobov, I.I., *Usp. Khim.,* 1996, vol. 65, no. 3, p. 195.
5. Kleperis, J., Wojcik, G., Czerwinski, A., et. al, *J. Solid State Electrochem.,* 2001, vol. 5, no. 4, p. 229.
6. Kazarinov, I.A. and Semykin, A.V., *Elektrodnye materialy na osnove gidridov metallov i splavov* (Electrode Materials on the Basis of Metal Hydrides and Alloys), Saratov: Saratov. Univ., 2005.
7. Rongeat, C. and Roue, L., *J. Electrochem. Soc.,* 2005, vol. 152, no. 7, p. A1354.
8. Kadir, K., Sakai, T., and Uehara, I., *J. Alloys Comp.,* 1997, vol. 257, p. 115; 1999, vol. 287, p. 264.
9. Kohno, T., Yoshida, H., Kawashima, F., Inaba, T., Sakai, I., Yamamoto, M., and Kanda, M., *Ibid.,* 2000, vol. 311, p. L5.
10. Pan, H., Liu, Y., Gao, M., Zhu, Y., Lei, Y., and Wang, Q., *J. Electrochem. Soc.,* 2004, vol. 151, no. 3, p. A374.
11. Vermeulen, P., Niessen, R.A.H., and Notten, P.H.L., *Electrochem. Comm.,* 2006, vol. 8, no. 1, p. 27.
12. Dhar, S.K., Ovshinsky, S.R., Gifford, P.R., Corrigan, D.A., Fetchenko, M.A., and Venkatesan, S., *J. Power Sources,* 1997, vol. 65, p. 1.
13. Liaw, B.Y. and Yang, X.-G., *Electrochim. Acta,* 2001, vol. 47, no. 6, p. 875.
14. Lee, S.-M., Park, J.-G., Han, S.-C., Lee, P.S., and Lee, J.-Y., *J. Electrochem. Soc.,* 2002, vol. 149, no. 10, p. A1278.
15. Skowronski, J.M., Sierczynska, A., and Kopczyk, M., *J. Solid State Electrochem.,* 2002, vol. 7, no. 1, p. 11.
16. Lupu, D., Biris, A.R., Biris, A.S., Indrea, E., Misan, I., Zuttel, A., and Schlapbach, L., *J. Alloys Comp.,* 2003, vol. 350, p. 319.
17. Majchrzycki, M. and Jurczyk, M., *J. Power Sources,* 2001, vol. 93, p. 77.
18. Kim, D.-M., Jang, K.-J., and Lee, J.-Y., *J. Alloys Comp.,* 1999, vols. 293–295, p. 583.
19. Zotov, T.A., Verbetsky, V.N., Safonova, T.Ya., and Petrii, O.A., *J. Solid State Electrochem.,* 2003, vol. 7, no. 9, p. 645.
20. Zhang, H. and Lei, Y., *Electrochim. Acta,* 2004, vol. 49, no. 15, p. 2503.
21. Xu, Y.H., Chen, Ch.P., Wang, X.L., and Wang, Q.D., *J. Power Sources,* 2002, vol. 112, p. 105.
22. Van Essen, R.H. and Buschow, K.H.J., *J. Less-Common Met.,* 1980, vol. 70, p. 189.
23. Chen, J., Takeshita, H.T., Tanaka, H., Kuriyama, N., Sakai, T., Uehara, I., and Haruta, M., *J. Alloys Comp.,* 2002, vol. 302, p. 304.
24. Tsirlina, G.A., Levi, M.D., Petrii, O.A., and Aurbach, D., *Electrochim. Acta,* 2001, vol. 46, p. 4141.
25. Noru, R. and Matsumoto, O., *J. Electrochem. Soc.,* 1996, vol. 143, p. 1919.
26. Gol'dshleger, N.F. and Moravskii, A.P., *Usp. Khim.,* 1997, vol. 67, p. 353.
27. Qin, X., Gao, X.P., Liu, H., et. al., *Electrochem. Solid State Lett.,* 2000, vol. 3, no. 12, p. 532.
28. Zuttel, A., Sudan, P., Mauron, Ph., et. al., *J. Alloys Comp.,* 2002, vol. 27, no. 2, p. 203.
29. Rajalakshmi, N., Dhathathreyan, K.S., Govindaraj, A., and Satishkumar, B.C., *Electrochim. Acta,* 2000, vol. 45, no. 27, p. 4511.
30. Frackowiak, E. and Beguin, F., *Carbon,* 2002, vol. 40, p. 1775.
31. Miranda-Hernandez, M., Ayala, J.A., and Rincon, M.E., *J. Solid State Electrochem.,* 2003, vol. 7, no. 5, p. 264.

32. Gaj, X.P., Wang, F.X., Liu, Y., Pan, G.L., Li, S., Qu, J.Q., Wu, F., Yuan, H.T., and Song, D.Y., *J. Electrochem. Soc.,* 2002, vol. 149, no. 12, p. A1616.
33. Jaksic, M., *Electrochim. Acta,* 1984, vol. 29, p. 1539; *Int. J. Hydrogen Energy,* 2001, vol. 26, no. 6, p. 559.
34. Ezaki, H., Morinaga, M., and Watanabe, S., *Electrochim. Acta,* 1993, vol. 38, no. 4, p. 557.
35. Yukawa, H., Nakatsuka, K., and Morinaga, M., *Solar Energy Materials and Solar Cells,* 2000, vol. 62, p. 75.
36. Morinaga, M., Yukawa, H., Nakatsuka, K., and Takagi, M., *J. Alloys Comp.,* 2002, vols. 330–332, p. 20
37. Varin, R.A. and Czujko, T., *Scripta Mater.,* 2002, vol. 46, p. 531.
38. Iwakura, C., Nohara, S., Furukawa, N., and Inoue, H., *Solid State Ionics,* 2002, vol. 148, p. 487.
39. Yang, C.-C. and Liu, S.-J., *J. Appl. Electrochem.,* 2003, vol. 33, no. 9, p. 777.
40. Iwakura, C., Kumagoe, K., Yoshiki, K., Nohara, S., Furukawa, N., Inoue, H., Minami, T., and Tatsumisago, M., *Electrochim. Acta,* 2003, vol. 48, no. 11, p. 1499.
41. Grigor'eva, T.F., Barinova, A.P., and Lyahov, N.Z., *Usp. Khim.,* 2001, vol. 70, no. 1, p. 52.
42. Berlouis, L.E.A., Comisso, N., and Mengoli, G., *J. Electroanalyt. Chem.,* 2006, vol. 586, no. 1, p. 105.
43. Anderson, M.L. and Anderson, I.E., *J. Alloys Comp.,* 2000, vol. 313, p. 47.
44. Shumin, H., Zhong, Z., Yuan, L., Tianfu, J., and Xiaofie, W., *Electrochim. Acta,* 2005, vol. 50, no. 28, p. 5491.
45. Li, L., Akiyama, T., and Yagi, J.-I., *J. Mater. Synth. Proces.,* 2000, vol. 8, p. 7.
46. Sokolov, V.V., Osadchaya, L.I., Safonova, T.Ya., and Petrii, O.A., *Elektrokhimiya,* 2002, vol. 38, no. 11, p. 1399.
47. Nan, J., Yang, Y., and Liu, Z., *J. Alloys Comp.,* 2001, vol. 316, p. 131; *Electrochim. Acta,* 2001, vol. 46, no. 12, p. 1767.
48. Ambrosio, R.C. and Ticianelli, E.A., *J. Electroanalyt. Chem.,* 2005, vol. 574, no. 2, p. 251.
49. Iwakura, C., Choi, W.-K., Zhang, S.G., and Inoue, H., *Electrochim. Acta,* 1999, vol. 44, no. 10, p. 1677.
50. Higuchi, E., Toyoda, E., Li, Z.P., Suda, S., Inoue, H., Nohara, S., and Iwakura, C., *Ibid.,* 2001, vol. 46, no. 8, p. 1191.
51. Tsukapara, M., Kamiya, T., Takahashi, K., Kawabata, A., Sakurai, S., Shi, J., Takeshita, H.T., Kuriyama, N., and Sakai, T., *J. Electrochem. Soc.,* 2000, vol. 147, no. 8, p. 2941.
52. Wu, M.-S., Wang, Y.-Y., and Wan, C.-C., *Ibid.,* 2000, vol. 147, no. 11, p. 4065.
53. Hariprakash, B., Martha, S.K., and Shukla, A.K., *J. Appl. Electrochem.,* 2003, vol.,33, no. 6, p. 497.
54. Chang, J.-K., Simon Shong, D.-N., and Tsai, W.T., *J. Solid State Electrochem.,* 2003, vol. 7, no. 8, p. 485.
55. Zhang, Y.-H., Chen, M.-Y., Wang, X.-L., Wang, G.-Q., Dong, X.-P., and Qi, Y., *Electrochim. Acta,* 2004, vol. 49, no. 7, p. 1161.
56. Pan, H., Ma, J., Zhu, Y., Li, S., Chen, Ch., and Wang, Q., *J. Alloys Comp.,* 2001, vol. 327, p. 136.
57. Folonari, C., Iemmi, G., Manfredi, F., and Rolle, A., *J. Less-Common Met.,* 1980, vol. 74, p. 371.
58. Chartouni, D., Kuriyama, N., Kiyobayashi, T., and Chen, J., *Int. J. Hydrogen Energy,* 2002, vol. 27, p. 945; *J. Alloys Comp.,* 2002, vols. 330–332, p. 766.
59. Vielstich, W., *Brenstoffelementen,* Weinheim: Chemie, 1965.
60. Nakano, H., Wakao, S., and Yoshinaga, H., *J. Alloys Comp.,* 1999, vols. 293–295, p. 698.
61. Marshall, J.H., *J. Electrochem. Soc.,* 1983, vol. 140, p. 369.
62. Lee, S.M., Kim, J.H., Lee, H.H., Lee, P.S., and Lee, J.Y., *Ibid.,* 2002, vol. 149, p. A603.
63. Li, Z.P., Liu, B.H., Arai, K., and Suda, S., *Ibid.,* 2003, vol. 150, p. A868.
64. Wang, L., Ma, Ch., Mao, X., Sheng, J., Bai, F., and Tang, F., *Electrochem. Commun.,* 2005, vol. 7, p. 1477.
65. Liao, B., Lei, Y.Q., Chen, L.X., Lu, G.L., Pan, H.G., and Wang, Q.D., *Electrochim. Acta,* 2004, vol. 50, no. 4, p. 1057.
66. Wang, Y., Gao, X.P., Lu, Z.W., Hu, W.K., Zhou, Z., Qu, J.Q., and Shen, P.W., *Ibid.,* 2005, vol. 50, no. 11, p. 2187.
67. Zhang, X.B., Sun, D.Z., Yin, W.Y., Chai, Y.J., and Zhao, M.S., *Ibid.,* 2005, vol. 50, nos. 16–17, p. 3407.
68. Ambrosio, R.C. and Ticianelli, E.A., *J. Solid State Electrochem.,* 2004, vol. 8, no. 8, p. 532.
69. Yang, X.-G. and Liaw, B.Y., *J. Electrochem. Soc.,* 2004, vol. 151, no. 1, p. A137.
70. Baddour-Hadjean, R., Pereira-Ramos, J.P., Latroche, M., and Percheron-Guegan, A., *Electrochim. Acta,* 2003, vol. 48, no. 19, p. 2813.
71. Yang, T.-H., Pyun, S.-I., and Goon, Y.-G., *Ibid.,* 1997, vol. 42, no. 11, p. 1701.
72. Pyun, S.-I. and Yang, T.-H., *J. Electroanalyt. Chem.,* 1998, vol. 441, nos. 1–2, p. 183; *Electrochim. Acta,* 1998, vol. 43, nos. 5–6, p. 471.
73. Lee, S.-J., Pyun, S.-I., and Lee, J.-W., *Electrochim. Acta,* 2005, vol. 50, no. 5, p. 1121.
74. Cabot, P.L., Guezala, E., Calpe, J.C., Garcia, M.T.,

and Casado, J., *J. Electrochem. Soc.,* 2000, vol. 147, no. 1, p. 43.

75. Lee, J.-W., Pyun, Su-Il, and Filipek, S., *Electrochim. Acta,* 2003, vol. 48, no.11, p. 1603.
76. Iwakura, C., Nohara, S., and Inoue, H., *Solid State Ionics,* 2002, vol. 148, p. 499.
77. Yuan, X. and Xu, N., *J. Appl. Electrochem.,* 2001, vol. 31, p. 1033.
78. Bernard, P., *J. Electrochem. Soc.,* 1998, vol. 145, no. 2, p. 456.
79. Maurel, F., Knosp, B., and Backhaus-Ricoult, M., *Ibid.,* 2000, vol. 147, no. 1, p. 78.
80. Wang, C.S., Marrero-Cruz, M., Baricuatro, J.H., Soriaga, M.P., Serafim, D., and Srinivasan, S., *J. Appl. Electrochem.,* 2003, vol. 33, nos. 3–4, p. 325.
81. Arnaud, O., Guenne, L.L., Audry, and C., Bernard, P., *J. Electrochem. Soc.,* 2005, vol. 152, no. 3, p. A611.
82. Liu, Y., Pan, H., Gao, M., Zhu, Y., Lei, Y., and Wang, Q., *Electrochim. Acta,* 2004, vol. 49, no. 4, p. 545.
83. Scnoh, H., Hara, Y., Inoue, H., and Iwakura, C., *Ibid,* 2001, vol. 46, no. 7, p. 967.
84. Vol'fkovich, Yu.M., Petrii, O.A., Zaitsev, A.A., and Kovrigina, I.V., *Vestn. Mosk. Gos. Univ. Ser. 2: Khim.,* 1988, vol. 29, p. 173.
85. Yang, X.-G. and Liaw, B.Y., *J. Electrochem. Soc.,* 2004, vol. 151, no. 2, p. A265.
86. Araki, T., Nakayama, M., Fukuda, K., and Onda, K., *Ibid.,* 2005, vol. 152, no. 6, p. A1128.
87. Gu, W.B., Wang, C.Y., Li, S.M., Geng, M.M., and Liaw, B.Y., *Electrochim. Acta,* 1999, vol. 44, no. 25, p. 4525.
88. Wu, B. and White, R.E., *J. Electrochem. Soc.,* 2000, vol. 147, no. 3, p. 902.
89. Wu, M.-S., Hung, Y.-H., Wang, Y.-Y., and Wan, C.-C., *Ibid.,* 2000, vol. 147, no. 3, p. 930.
90. Gu, W.B. and Wang, C.Y., *Ibid.,* 2000, vol. 147, no. 8, p. 2910.
91. Subramanian, V.R., Ploehn, H.J., and White, R.E., *Ibid.,* 2000, vol. 147, no. 8, p. 2868.
92. Jiang, J.-J., *J. Appl. Electrochem.,* 2003, vol. 33, no. 1, p. 101.
93. Nan, J., Han, D., Yang, M., and Cui, M., *J. Electrochem. Soc.,* 2006, vol. 153, p. A101.

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