



Short communication

Oxygen and hydrogen gas recombination in NiMH cells

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ABSTRACT

The kinetics of oxygen and hydrogen gas recombination on the metal hydride electrode in a NiMH cell is investigated as function of gas pressure, temperature, cycling and a hydrophobic additive. Both oxygen and hydrogen gas recombination rates in the NiMH cells are found to be linearly proportional to the gas pressure, indicating that surface processes with a constant number of reaction sites could be the rate limiting step. The rate of oxygen gas recombination is, however, more than 10 times faster than that of hydrogen at the same pressure. As the temperature increases, both reaction rates increase very rapidly, even though the solubilities of the gases in the KOH electrolyte decrease with temperature. The activation energies for oxygen and hydrogen gas recombination are 32.6 kJ mol^{-1} and 27.0 kJ mol^{-1} , respectively. The reactions rates also increase as the cells are cycled. This indicates, that the number of active sites increases, as the surface area increases, due to the continuously decrepitating of the alloy particles. The hydrogen gas absorption rate increases dramatically after a large number of cycles due to the drying of the MH electrode. A hydrophobic PTFE additive in the MH electrode can significantly improve hydrogen absorption efficiency in NiMH cells.

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1. Introduction

The NiMH battery has already found wide use in various applications and is the dominant chemistry for hybrid electric vehicles (HEV). In contrast to electric vehicle batteries it is possible to reduce the critical battery cost, which is proportional to the driving range, by reducing the battery size if the power rating can be improved. This demanding application needs, however, batteries with long cycle life and very rapid charge and discharge capabilities. During charge and discharge the electrodes interact with each other through the alkaline electrolyte, as hydrogen is transported in the form of water molecules between the electrodes. During discharge hydrogen is released from the negative metal hydride electrode, and migrates to the positive nickel hydroxide electrode where it is intercalated and binds to an oxygen atom, releasing the stored energy. During charging the oxygen–hydrogen bond is broken and the direction of the hydrogen transport is reversed.

The electrodes are, however, also interacting with each other via the gas phase. If these gas phase reactions are properly controlled, they can help to keep the charge state of all cells in a battery pack in phase, and also help to protect the MH electrode during over-discharging. In practice this is made by having nickel electrode limited sealed NiMH cells with a starved electrolyte. This means that the capacity of the positive nickel electrode is lower than the

negative MH electrode and the amount of electrolyte is so low, that open porosity still remains in the separator, allowing for gases to pass between the electrodes.

The nickel oxide electrode will start to emit oxygen at the end of the charge. This is expected in a sealed cell as a consequence of the intentionally limited capacity of the positive nickel electrode. Limitation in the charge efficiency of the positive electrode can, however, also lead to oxygen evolution earlier in the charge cycle, especially at high temperatures and at very high charging currents. The capability of the metal hydride electrode to recombine the evolved oxygen from the positive electrode limits the maximum charge current that can be applied. When the cell is over discharged, on the other hand, the limited capacity of the nickel electrode will lead to a corresponding evolution of hydrogen. But a poor charge acceptance of the MH electrode at high temperatures and high charge as well as high discharge rates can, however, also lead to a hydrogen pressure increase in the cell. Abusive use of the cell can under certain conditions lead to a dangerous mixture of hydrogen and oxygen in the cell. NiMH cells can in contrast to the NiCd cell recombine this hydrogen at the MH electrode. Anyhow, the battery cycle life will be limited, if the pressure build-up in the cell is vented through the safety-valve, as this can quickly dry out the cell. There have been many efforts to reduce the gas evolution problem, for example, by using additives to the Ni(OH)_2 , by surface coating of the metal hydride alloy or by alkaline etching of the alloy surface to form a Ni-rich catalytic surface [1–4]. There are, however, a limited number of publications about the kinetics of oxygen gas recombination and hydrogen gas absorption

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at the metal hydride electrode in NiMH cells. Yan studied oxygen gas recombination in cells using a TiNi alloy as negative electrode and concluded that metallic clusters of Ni atoms exhibit high catalytic activity in the recombination reaction [5]. Wu et al. used gas chromatography to show that gaseous hydrogen is the dominant component responsible for the inner pressure rise, and that smaller metal hydride particles with a corresponding larger surface area at the MH electrode facilitated a quicker recombination of the hydrogen gas [6]. Liaw and Yang showed that the rapid rechargeability of some commercial NiMH batteries exceeded the guidelines set by the DOE/USABC Battery Test Procedure Manual [7]. Without going into details of the gas evolution mechanism they found, however, that strict control of the charging/discharging algorithm is needed to avoid excessive pressure build up and subsequent venting and drying out of the cells. More recently Cuscueta et al. undertook a study of the pressure rise in a specially designed sealed NiMH test cell, where the electrochemically characterisation could be done while simultaneously recording the inner cell pressure [8]. They could also confirm an excessive pressure build up at high rates, which needed a well controlled charging/discharging algorithm to avoid deterioration of the cell.

By following the time dependence of how small gas additions are recombined in a sealed NiMH cell, we will here report quantitative results of the effect of pressure, temperature, cycling and some additives on the kinetics, in order to describe both oxygen and hydrogen recombination reactions. A better understanding and control of these reactions is necessary for further increasing the power output of NiMH batteries and to construct more effective charging/discharging algorithms.

2. Experimental details

Cells used in this test were of sub-C size, and the electrodes were made by a dry powder method, from about 15 g of an AB₅ alloy with the standard composition $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ and 6 g of 6 M KOH + 1 M LiOH electrolyte [9]. The nominal cell capacity was 2.3 Ah. A special pressurised cell holder schematically shown in Fig. 1 was designed for this investigation. The cell within the holder could be electrically charged and discharged, pure hydrogen or oxygen could also be filled from outside into the pressure cell through a valve. This allowed us to study pure oxygen recombination or pure hydrogen gas absorption in the cells at different states of charge. A pressure transducer and a PC-system recorded pressure changes vs. time. The total void volume in the pressure cell was about 8.2 cm³, including the void volume in the sub-C cell of

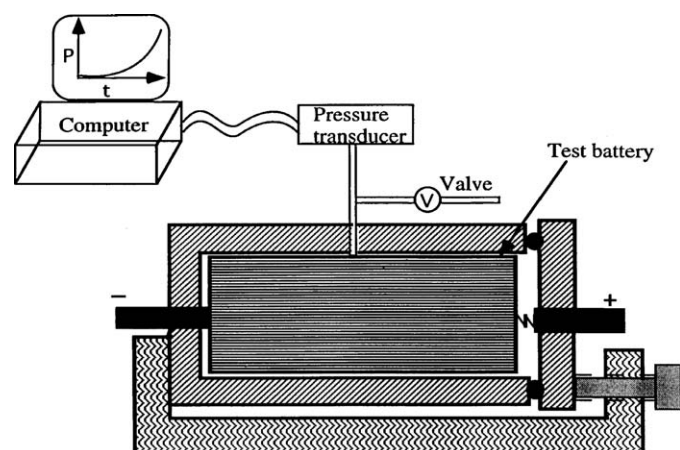


Fig. 1. Schematic drawing of the measuring system for monitoring the gas pressure in simulated sealed cells.

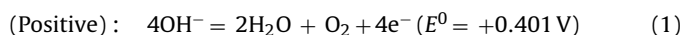
about 5 cm³. The total void volume was used to calculate the moles of gas assuming ideal gas behaviour of the gases.

In order to study the effect of polytetrafluoroethylene (PTFE) addition on the gas recombination, 0.2 g of PTFE (ca. 1 wt% of total negative electrode weight) was mixed with MH alloy powder before making the cells. In order to study the effect of cycling on gas reaction rate, several sealed cells were cycled a number of times before they were opened for gas reaction tests. Before this activation the air was removed by evacuating the cells for a few seconds using a vacuum pump. Fully charged cells were rested for several hours after charging, so that the gases produced during overcharge would be completely consumed by the MH electrode before they gas kinetic reaction were investigated.

3. Results and discussion

3.1. Oxygen gas recombination

Oxygen gas can be produced on the Ni electrode during overcharge according to:



If the charge efficiency is low, this reaction can also occur especially at high temperatures or at high charge rates. The oxygen diffuses through the separator to the MH electrode, where it recombines chemically producing water according to Eq. (2), thus preventing an excessive pressure rise in the cell.



The oxygen gas pressure during overcharge in the cell will depend on the rate difference of these two reactions. The rate of the first one depends mainly on the overcharge current. Interesting for us would be to improve the kinetics of the second reaction. The mechanism of oxygen recombination is rather complicated. The alloy powder is covered by a thin electrolyte layer, making it a gas–liquid–solid reaction system. The oxygen must solve in the electrolyte, diffuse through an electrolyte layer and be transferred from the liquid to the solid surface. This process involves a gas–liquid interface and a liquid–solid interface.

After 10 activation cycles, a cell was full charged and rested for several hours after which we applied pure oxygen gas into the pressure cell, and recorded the change of the gas pressure with time. The results are shown in Fig. 2. The curve of pressure vs. time shows a typical exponential decay (Eq. (3)). The measured data (dots) fit well to a single exponential function with an *R*-value very close to 1. *P* varies as:

$$P = P_0 e^{-at} \quad (3)$$

Here *P* and *P*₀ are the gas pressure in the cell at time *t* and *t*=0, respectively, and *a* [min⁻¹] is a constant. This means that reaction

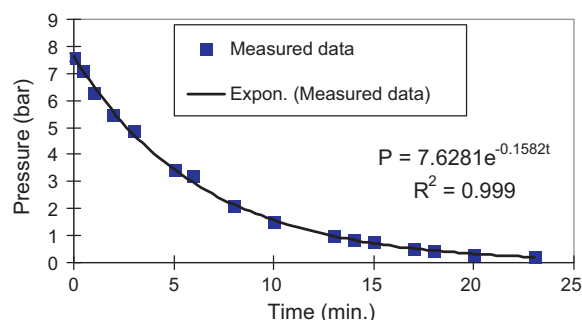


Fig. 2. Oxygen pressure vs. time in a NiMH cell at room temperature.

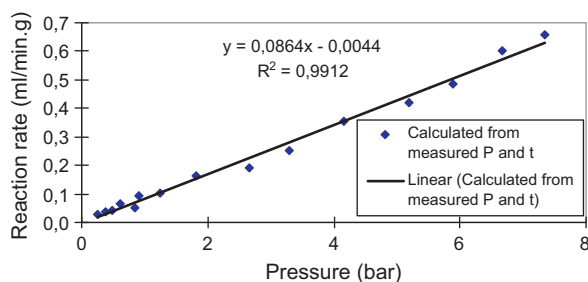


Fig. 3. Oxygen gas recombination rate vs. gas pressure in a NiMH cell at room temperature.

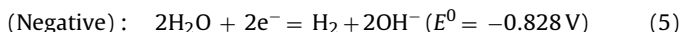
rate is proportional to the gas pressure P , as seen in Fig. 3. The reaction rate (r) can be described by Eq. (4).

$$r = \frac{(dP/dt) \times V}{W \times P_{SAPT}} = \frac{-a \times P \times V}{W \times P_{SAPT}} \quad (4)$$

Here V is the total internal volume of the pressure cell and W is the weight of the metal hydride alloy and P_{SAPT} is at the Standard Ambient Temperature Pressure. This may be interpreted as evidence that a surface process is the rate-limiting step. Oxygen gas has a low solubility in a KOH electrolyte. This is about 1.91×10^{-6} (mole fraction) at 1 bar gas pressure. The low solubility of oxygen in the thin film of electrolyte covering the particle could be one cause of the slow recombination rate. When the pressure increases up to 10 bar, the oxygen gas recombination rate is about 0.86 ml per minute and per gram of alloy, which corresponds to 1.5 C charge current. This means that the cell can be overcharged continuously at a 1.5 C rate without exceeding an oxygen pressure of 10 bar, assuming that no hydrogen gas is produced, and that the cell is effectively cooled to avoid over heating.

3.2. Hydrogen gas absorption

In a sealed NiMH cell, the metal hydride electrode is designed to have a higher capacity than the Ni electrode (the so-called charge capacity reserve). If both electrodes have good charge efficiency, only oxygen gas would be produced during overcharge as described above. If the charging rate is too high to form a hydride, a sub-reaction evolving hydrogen gas can occur (Eq. (5)).



Degradation of the metal hydride alloy by corrosion during cycling can also cause hydrogen evolution in the sealed batteries. The decomposition of the alloy into mainly mischmetal hydroxides and nickel powder produces extra hydrogen which offsets the balancing of the electrodes in the cell and reduces charge capacity reserve. Hydrogen gas can also be produced on the Ni-electrode during overdischarge. The produced hydrogen gas should be absorbed by the metal hydride in the negative electrode in order to prevent gas accumulation during cycling. Similar to the study of oxygen gas recombination, we also recorded the change of pure hydrogen pressure vs. time. Also in this case we obtained an exponential function of pressure vs. time as seen in Fig. 4. This shows us that the limiting step of this reaction is also a surface process. The hydrogen absorption rate calculated by Eq. (4), was however, much slower than the rate of the oxygen gas combination, which can be seen by comparing Fig. 5 with Fig. 3. This is interesting, as the mass transfer processes from the gas phase to the alloy surfaces in both reaction systems ought to be similar. The solubility of hydrogen gas in the KOH electrolyte at room temperature is about 2.4×10^{-6} (mole fraction) at 1 bar gas pressure, which is even a little better than the solubility of oxygen. The linear dependence of the absorption rate on the gas pressure is also similar to dry

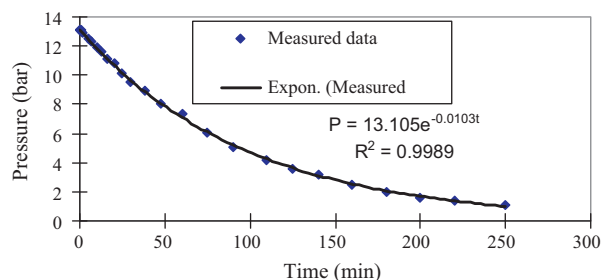


Fig. 4. Hydrogen pressure vs. time in a NiMH cell at room temperature.

hydrogen absorption containing some impurities such as CO, CO₂ and NH₃ as described in Ref. [10]. The hydrogen absorption rate in the gas–liquid–solid system of the cell is much slower than that in the gas–solid system. For example, at room temperature and a 10 bar gas pressure, the hydrogen absorption rate on the metal hydride electrode is about 0.054 ml per minute and per gram of alloy instead of the 44 ml min⁻¹ per gram alloy rate for a LaNi₅ alloy absorbing hydrogen with an 0.1% CO₂ impurity [10]. On the other hand, in hydrogen–metal hydride alloy (gas–solid) system, the reaction rate is related to the HM^{-1} value, and is therefore much faster at the beginning (low HM^{-1} value) and becomes slow at last stage (MH close to 1). In the battery, the absorption rate during discharge (HM^{-1} is about 0.13) is, however, very close to that during charge (HM^{-1} is about 0.63) as shown in Fig. 5, further indicating, that surface and not bulk effects are responsible for the main rate determining step. A very low solubility of hydrogen in the KOH electrolyte and a degradation of catalytic H–H bond breaking mechanism due to H₂O and OH⁻ ions blocking the alloy surface will probably be the main reasons for the slow reaction rate. The 0.054 ml min⁻¹ g⁻¹ rate corresponds to only a 0.05 C current rate. This means that if we use 1 C rate to charge the battery and the charge efficiency is lower than 95%, the hydrogen pressure in cell will gradually rise to the opening pressure of the safety valve. It will take several hours to consume the hydrogen produced and stored in the cells during resting and discharging. This was further illustrated by adding a mixture of oxygen and hydrogen to the cell. The presence of hydrogen that is getting concentrated in the porous structure in the electrode slows down the oxygen recombination, leading to a slow and complex time evolution of the gas decrease with time. The large rate difference between hydrogen absorption and oxygen recombination shows us that it is very important to keep good charge efficiency in the metal hydride electrode in order to retain a good overcharge protection in the NiMH cell. This is very important for high voltage applications such as in HEV, with many cells connected series, making it necessary to improve the hydrogen absorption rate in the cells. During overdischarge, 100% of current will be used to produce hydrogen at the positive electrode, which must be absorbed in the MH electrode.

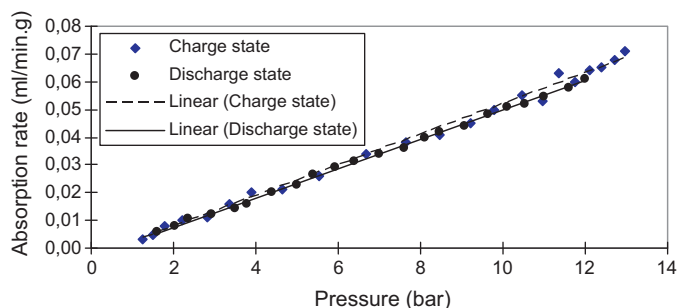


Fig. 5. Hydrogen absorption rate during charge and discharge vs. gas pressure in a NiMH cell at room temperature.

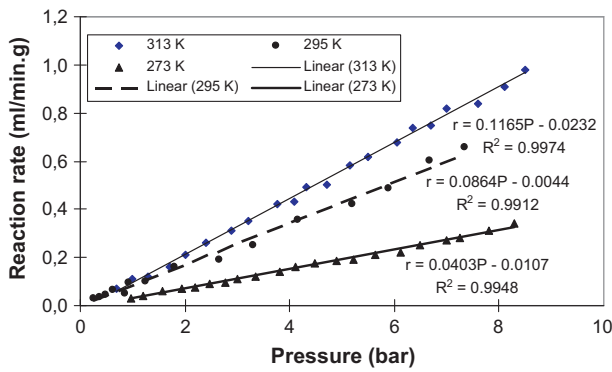


Fig. 6. Oxygen gas recombination rate vs. gas pressure in a NiMH cell at different temperatures.

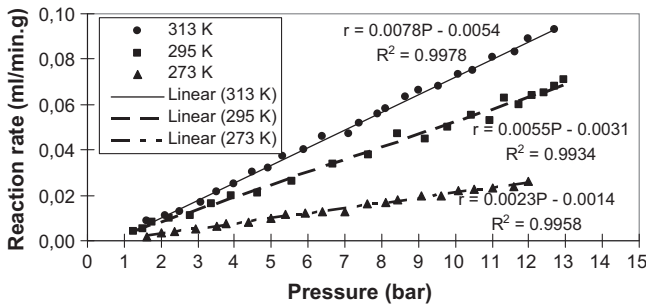


Fig. 7. Hydrogen absorption rates vs. gas pressure in a NiMH cell at different temperatures.

3.3. The effect of temperature on reaction rates

Both the oxygen gas recombination and hydrogen absorption rate were measured at different temperatures. The results are shown in Fig. 6 for oxygen and in Fig. 7 for hydrogen. We can find from the figures that the reaction rates increase very fast as the temperature rises. As discussed before, the reaction rate is proportional to pressure according to Eq. (6). Because the solubility of gas in the electrolyte depends linearly on the gas pressure according to Henry's Law (Eq. (7)), the reaction rate is actually proportional to the concentration (Eq. (8)).

$$r = k_p \times P \quad (6)$$

$$P = k_H \times C \quad (7)$$

$$r = k_p \times k_H \times C = k \times C \quad (8)$$

Here k_p is an empirical rate coefficient from the slope of the r vs. P diagrams, k_H is Henry's law constant, and k is a reaction rate constant which can be assumed to have an Arrhenius behaviour by Eq. (9):

$$k = A \times e^{(-E_a/RT)} \quad (9)$$

Here E_a is the activation energy, R is the gas constant, T is the temperature and A is the frequency factor. Henry's constant is related to temperature, and the solubility decreases as temperature increase at a constant pressure. This means that the temperature can affect the reaction rate in two ways. As temperature increases, the reaction rate constant increases giving a positive contribution. The gas solubility, however, decreases which will have a negative effect. The k values can be calculated from multiplying k_p in Figs. 5 and 6 with k_H from Refs. [11,12]. The values are listed in Table 1.

In Fig. 8 $\ln(k)$ is plotted vs. $1/T$ for oxygen recombination and for hydrogen absorption. From this we get an activation energy of 32.6 kJ mol^{-1} for the oxygen recombination and the about

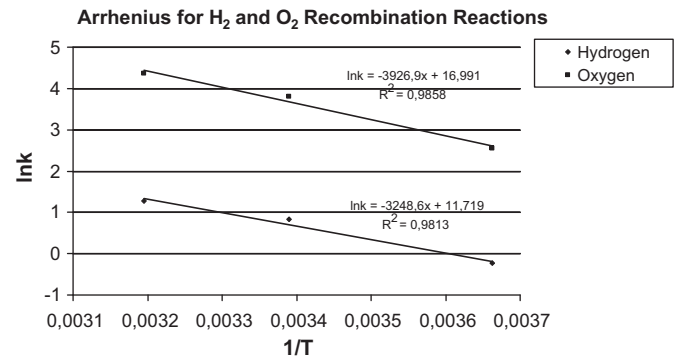


Fig. 8. Arrhenius plots for oxygen recombination and hydrogen absorption in a NiMH cell.

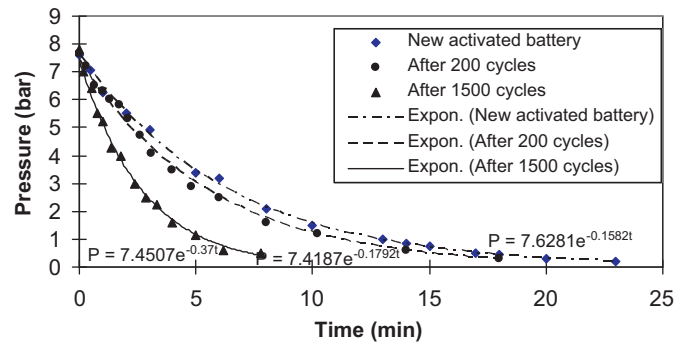


Fig. 9. Oxygen gas pressure vs. time in cycled NiMH cells at room temperature.

27.0 kJ mol^{-1} for hydrogen absorption. The high activation energies lead to a significant increase of the reaction rates with temperature, even though the solubility of both gases in the KOH electrolyte decreases.

3.4. Gas reactions in long time cycled batteries

The gas reactions in cycled cell were investigated as well. Two groups of cycled cell were tested. One was cycled 200 times, retaining almost the same capacity and other properties as in newly activated cells. The other group of cells was cycled 1500 times. Their discharge capacity was reduced to 1.6 Ah, and also other properties such as the rate capability had deteriorated markedly. By measuring the discharge capacity of metal hydride alloy in half cell after gas reactions test, it was found that the alloy from the long time cycled cells had lost about 45% of the initial capacity. The pressure changes with time in cycled cells for oxygen recombination and hydrogen absorption are compared with those of newly activated cells in Figs. 9 and 10, respectively. After 200 cycles, the rates for both reactions had increased with about 20%, which might

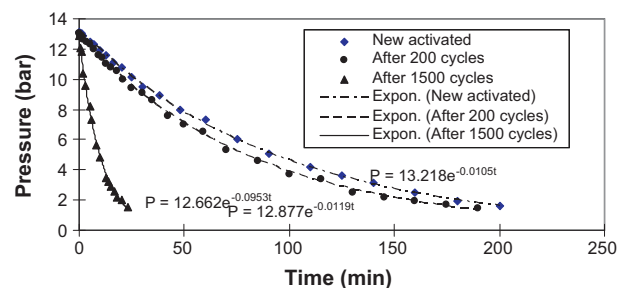


Fig. 10. Hydrogen gas pressure vs. time in cycled NiMH cells at room temperature.

Table 1
Kinetic parameters of oxygen recombination and hydrogen absorption reactions.

Temperature (K)	Oxygen, k_p (ml min ⁻¹ g ⁻¹ bar ⁻¹)	k_H (bar dm ³ mol ⁻¹)	k (l min ⁻¹)	Hydrogen, k_p (ml min ⁻¹ g ⁻¹ bar ⁻¹)	k_H (bar dm ³ mol ⁻¹)	k (l min ⁻¹)
273	0.0403	5671	12.9	0.0023	6133	0.794
295	0.0864	9262	44.1	0.0055	7413	2.29
313	0.1165	12071	78.9	0.0078	8107	3.56

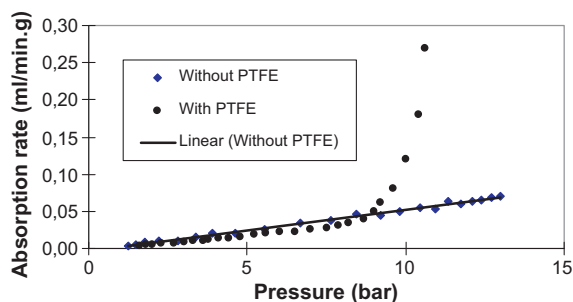


Fig. 11. Hydrogen absorption rate vs. gas pressure in NiMH cells with and without PTFE at room temperature. Figures for “Oxygen and Hydrogen Gas Recombination in NiMH Cells”.

be due to the increase of total reaction area of the metal hydride. After 1500 cycles, the oxygen gas recombination rate had increased with a further 100%. Interestingly the hydrogen absorption rate had increased about 10 times compared to a newly activated cell. The main reason for this dramatic increase may be that the amount of electrolyte in the metal hydride electrode had been reduced after long cycling. The electrolyte depletion was verified after the experiment by the fact that the cell rate capability was substantially recovered by refilling electrolyte into the cycled cell. The large difference in the behaviour of the oxygen and hydrogen shows that hydrogen absorption reaction is more sensitive to the thickness of the electrolyte film covering the alloy particles. This leads us to start to experiment with additives to the metal hydride electrode in order to reduce the electrolyte covering of the alloy particles further.

3.5. The effect of PTFE on hydrogen absorption

PTFE has been used as a binder material in metal hydride electrodes to reduce the loss of alloy powder particles from the electrode [2]. PTFE is a hydrophobic polymer, and we therefore assumed that if we mixed some of it with the hydride alloy powder; we could reduce the electrolyte covering on alloy particles and thereby improve the hydrogen absorption rate. Some primary test results are shown in Fig. 11. The curve has two parts. At high pressure, immediately after the addition of hydrogen gas, the hydrogen absorption rate is much faster than that in the cell without PTFE. At lower pressure, the reaction rate, however, becomes somewhat slower than that in the cell without PTFE. We think that there are two kinds of metal hydride powders in the MH electrode, namely one with a partial PTFE coverage and another without. The first part of curve mainly reflects the hydrogen absorption by alloy powders with PTFE covering, which soon becomes saturated. The second part of curve would thus be due to hydrogen absorption by alloy powder without PTFE. The result shows that PTFE does have a very positive effect on the hydrogen absorption in the metal hydride electrode, but that a large addition will worsen the electrode's electrochemical performance by the decreasing the active surface. If only a small part of alloy particles is reached by the PTFE additive, it will restrict the amount of hydrogen that can be absorbed fast. So the ideal

situation would be for each of the particles to have a small fraction of its surface area covered by PTFE, allowing the whole of the alloy to participate in the fast hydrogen absorption. We could not find any significant difference of oxygen gas recombination between our tested cells with and without PTFE additive. This can indicate that there are different species active in the recombination of the two gases. More detailed work needs to be done to optimise the addition of hydrophobic additives in MH electrodes.

4. Conclusions

Both the oxygen gas recombination rate and the hydrogen absorption rate in NiMH cells were found to be linearly dependent on the gas pressure. This shows that some surface process is the rate limiting step. The rate of oxygen gas recombination at a 10 bar gas pressure is about 0.86 ml per minute per gram of alloy and the hydrogen absorption rate at the same pressure is only about 0.055 ml min⁻¹ g⁻¹ of alloy. This verifies in some way the findings of Wu et al. that hydrogen gas is dominating in the cells. Not because it is formed in excess, but when it is once produced, it is difficult to eliminate it from the inner cell volume. As the temperature increases, the rates of both reactions increase, even though the gases solubility in the electrolyte decreases. The activation energies for oxygen gas recombination and hydrogen absorption were 32.6 kJ mol⁻¹ and 27.0 kJ mol⁻¹, respectively. Both gas reaction rates increase as cells are cycled. The hydrogen gas absorption rate increase dramatically after a large number of cycles due to the electrolyte drying of the MH electrode. Hydrophobic additives to the MH electrode can dramatically improve hydrogen absorption efficiency in NiMH cells and open up for more effective high rate batteries.

Acknowledgment

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References

- [1] M. Oshitani, H. Yufu, K. Takashima, S. Tsuji, Y. Matsumora, J. Electrochem. Soc. 136 (1989) 1590.
- [2] T. Sakai, A. Yuausa, H. Ishikawa, H. Miyamura, N. Kuriyama, J. Less-Common Met. 172/174 (1991) 1175–1184.
- [3] M. Kanda, M. Yamamoto, K. Kanno, Y. Satoh, H. Hayashida, M. Suzuki, J. Less-Common Met. 172/174 (1991) 1227–1235.
- [4] H. Ogawa, M. Ikoma, H. Kawano, I. Matsumoto, J. Power Sources 12 (1989) 393–410.
- [5] D.Y. Yan, J. Alloys Compd. 209 (1994) 257–261.
- [6] J. Shi, F. Wu, D. Hu, S. Chen, L. Mao, G. Wang, J. Power Sources 161 (2006) 692–701.
- [7] X.G. Yang, B.Y. Liaw, J. Power Sources 101 (2001) 158–166.
- [8] D.J. Cuscueta, H.R. Salva, A.A. Ghilarducci, J. Power Sources 196 (2011) 4067–4071.
- [9] Z. Ye, T. Sakai, D. Noréus, E. Rosén, N.E. Barring, J. Electrochem. Soc. 142 (12) (1995) 4045.
- [10] P.D. Goodwell, P.S. Rudman, J. Less-Common Met. 89 (1983) 117.
- [11] C.L. Young, IUPAC, Solubility Data Series, vol. 5/6, Hydrogen and Deuterium, Pergamon Press, Oxford, England, 181.
- [12] R. Battino, IUPAC, Solubility Data Series, vol. 7, Oxygen and Ozone, Pergamon Press, Oxford, England, 181.