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Influence of the Nb_2O_5 distribution on the electrochemical hydrogenation of nanocrystalline magnesium

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Abstract

Nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst was studied as an electrode material for electrochemical hydrogen charging in a 6 M KOH electrolyte. A strong influence of the compaction parameters, the current density and the catalyst on the hydrogenation behavior was observed. The addition of graphite and PTFE to the Mg/Nb_2O_5 electrodes improves the charging kinetics as well as the hydrogen content. The hydrogen contents achieved in Mg with Nb_2O_5, however, show a broad scatter. It was concluded that the catalyst distribution influences the upper limit of the storage capacity as well as the oxidation process at the surface during preparation. Since the addition of Nb_2O_5 was observed to reduce the hydrogen overpotential of Mg depending on the catalyst distribution, it is assumed that the catalyst influences the electrode reactions. Therefore, hydrogenation was investigated for different Nb_2O_5 distributions at different current densities in detail.

Keywords: Magnesium; Nanocrystalline; Catalyst; Hydrogen absorbing materials; Electrochemical reactions

1. Introduction

During the last decades investigations were conducted on the improvement of hydrogen storage electrodes for battery applications [1–3]. Nanocrystalline Mg-based metal hydrides are considered to be important candidates for safe energy storage and transport material. But due to still high sorption temperatures and unknown cycling life commercialization in mobile storage systems, metal/hydride batteries and other clean applications slowed down. Recently it has been published that for hydrogenation from the gas phase the design of improved nanocrystalline Mg alloys can proceed by the addition of metal oxides, e.g. Nb_2O_5, as catalysts [4–7]. However these studies have focused only on the hydriding characteristics of nanocrystalline Mg with the addition of metal oxides in the gas phase. In order to verify whether such an addition improves also electrochemical hydrogenation, nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst as an electrode material for electrochemical hydrogen charging processes electrolyte was studied in a 6 M KOH [8,9]. These investigations revealed a strong influence of the compaction parameters, the current density and the catalyst on the hydrogenation behavior at low current densities. With decreasing current density the storage capacity as well as the kinetics of Mg/Nb_2O_5 electrodes increased significantly up to 1 wt.% H_2 at a charging time of 30 min. Since the hydrogen overpotential of Mg, which is a measure of the hydrogen evolution at the electrode surface, was observed to be reduced by the addition of Nb_2O_5, it is assumed that the catalyst influences the electrode reactions. The aim of this paper is to present further results on the influence of the Nb_2O_5 distribution on electrochemical hydrogenation of nanocrystalline Mg.

2. Experimental

Mg powder without and with 2 mol% Nb_2O_5 as a catalyst was prepared by milling MgH_2 (Goldschmidt AG, 95% purity, the rest being magnesium) using a planetary ball mill (Fritsch P5) with a ball to powder weight ratio of 400 g/40 g and subsequent desorption of the MgH_2 powders at 300 °C. 2 mol% Nb_2O_5 powder was added after milling MgH_2 for 20 h and blended by milling for additional 100 h. The observed hydrogen content after thermal desorption was 0.15 wt.% H_2. The powder was used to design a proper electrode for electrochemical hydrogenation which provides good mechanical stability and good conductivity to allow the dissociation and adsorption of hydrogen at the surface as well as diffusion into the material. The Mg electrodes were prepared by compaction at different pressures without any additions as well as with 5 wt.% graphite and 5 wt.% PTFE. Since Mg is highly reactive in oxygen the preparation of the powders, including milling and electrode preparation, was performed in a glove box under a continuously purified Ar atmosphere. Cathodic hydrogena-

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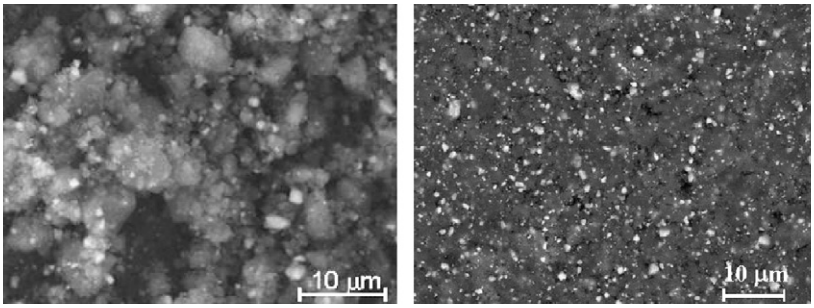

Fig. 1. SEM of Mg-powder with (a) inhomogenous and (b) homogenous Nb_2O_5 catalyst distribution.

tion was carried out in a 6 M KOH electrolyte at 25 °C and a current density between $i = 50$ and 5 mA/g. Further electrochemical measurements such as determining the overvoltage were performed under the same electrolyte conditions. The potential was measured and plotted against the potential of a Hg/HgO electrode. The hydrogen content was measured by a hydrogen determinator (RH-404, Leco). Morphology, catalyst distribution and microstructure of the Mg powder with and without Nb_2O_5 were investigated by X-ray diffraction and SEM.

3. Results and discussion

Microstructural investigations by SEM (Fig. 1) of desorbed MgH_2/2 mol% Nb_2O_5 powder showed a Mg particle size of 5–10 μm and a Nb_2O_5 particle size of 1–4 μm. The distribution of the Nb_2O_5 catalyst of the investigated Mg/Nb_2O_5 electrodes varied from inhomogenous to homogenous. The grain size of the Mg/Nb_2O_5 powder was found to be 50–200 nm [9].

As reported earlier [9] a strong influence of the Nb_2O_5 catalyst was observed with decreasing current densities. The results (Fig. 2) for the Mg electrodes show a high accuracy in comparison to a broad scattering for the Mg/Nb_2O_5 electrodes (grey shaded area). The observed hydrogen contents varied between 0.25 and 1.0 wt.% for the Mg/Nb_2O_5 electrodes. However, a strong influence of the catalyst was observed with decreasing current densities for the upper hydrogen charging limit. While the storage capacity of about 0.4 wt.% H_2 of the Mg-electrode changes only by a small amount to lower hydrogen contents of 0.35 wt.% with decreasing current density, the storage capacity as well as the kinetic of Mg/Nb_2O_5 electrodes increased significantly up to 1 wt.% H_2 at a charging time of 30 min with decreasing current density.

The upper limit and the scattering of the storage capacity might be influenced by the catalyst distribution. Therefore, Mg/Nb_2O_5 electrodes with a homogenous catalyst distribution were hydrogenated at different current densities (Fig. 3) in comparison to the inhomogenous Nb_2O_5 distribution (Fig. 2). Fig. 3 exhibits that the results for the Mg/Nb_2O_5 electrodes with a homogeneous catalyst distribution show a higher accuracy in comparison to the broad scattering in the other case. But as compared to the inhomogeneous catalyst distribution the homogeneous distribution results not only in a better reproducibility of the hydrogen content but also to a reduced kinetic. This might be due to a change in the overpotential with the catalyst distribution and/or accelerated oxidation processes by the catalyst at the surface during preparation.

Potentiodynamic polarization experiments (Fig. 4) gave additional information regarding the surface reactions at the electrode, specially regarding the hydrogen overvoltage of the investigated electrodes. In general it was observed that Nb_2O_5 decreases the hydrogen overvoltage $\eta_{2.5}$ of Mg compacted at a compaction pressure of 6.2 N/mm^2. As reported earlier [8] no significant influence of the addition of graphite as well as PTFE on the hydrogen overvoltage was observed. The reduced

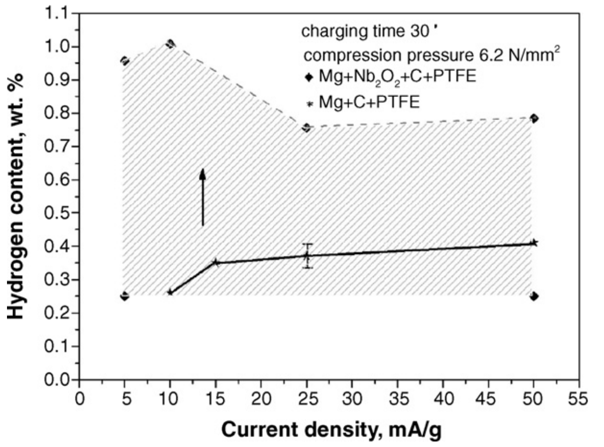

Fig. 2. Influence of the current density after charging for 30 min on inhomogenous distributed Nb_2O_5 in Mg/Nb_2O_5-electrodes compacted with a suspension of graphite and PTFE at a compaction pressure of 6.2 N/mm^2.

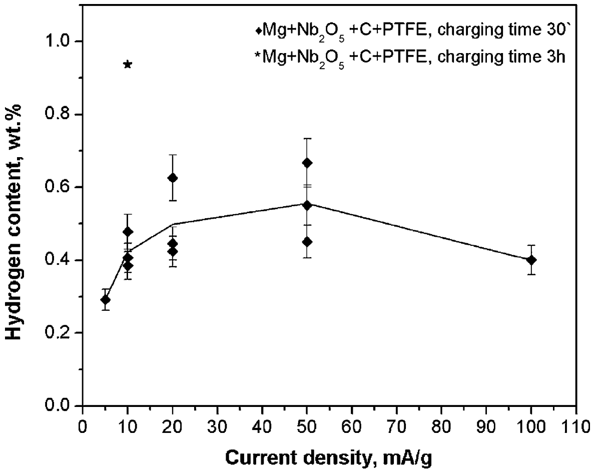

Fig. 3. Influence of the current density after charging for 30 min on homogenous distributed Nb_2O_5 in Mg/Nb_2O_5-electrodes compacted with a suspension of graphite and PTFE at a compaction pressure of 6.2 N/mm^2.

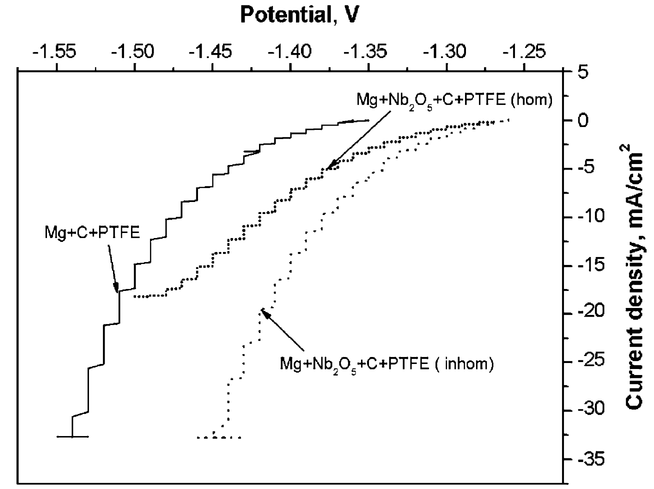

Fig. 4. Influence of the catalyst distribution on potentiodynamic polarization of the Mg and Mg/Nb_2O_5-electrodes compacted with a pressure of 6.2 N/mm^2.

hydrogen overvoltage due to the catalyst is assumed to accelerate the hydrogen evolution at the electrode surface and explains the independence of the addition of the catalyst on the hydrogen content at 50 mA/g and a charging time of 30 min for both distributions. At lower current densities it is assumed that the Volmer reaction $H_2O + e^- \rightarrow H_{ad} + OH^-$ will become the speed limiting reaction and the competing hydrogen recombination reactions will be irrelevant for the Mg/Nb_2O_5 electrodes. It is assumed that at very low current densities the electrochemical equilibrium is moved to the anodic reaction and leads to a lower storage capacity of the Mg/Nb_2O_5 electrodes because of an increased oxidation in the 6 M KOH electrolyte.

In addition Fig. 4 reveals a significant higher hydrogen overpotential for the homogenous in comparison to the inhomogenous catalyst distribution; thus might explain the lower hydrogen content and slower kinetic. It is assumed that the differences of the catalyst distribution and therefore in the hydrogen overpotential indicate a major influence of the oxidation behavior during the electrode preparation and/or the Nb_2O_5/Mg interfaces on the hydrogenation. There is evidence for the formation of an oxide layer at the interfaces during ball milling [10] which could explain the differences of the electrochemical hydrogenation behavior depending on the catalyst distribution. Further microstructural and electrochemical investigations are underway and should clarify the effect of Nb_2O_5 on the charging behavior of nanocrystalline Mg in more detail.

4. Conclusion

Nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst compacted with a suspension of graphite and PTFE at a compaction pressure of 6.2 N/mm^2 was studied in a 6 M KOH as an electrode material for electrochemical hydrogen charging processes electrolyte. A strong influence of the Nb_2O_5 catalyst on the electrochemical surface reaction was observed with decreasing current densities.

Nb_2O_5 reduces the hydrogen overvoltage of Mg compacted at a compaction pressure of 6.2 N/mm^2. A homogeneous catalyst distribution results not only in a better reproducibility of the hydrogen content but also to a slower kinetic in comparison to an inhomogenous distribution. It is shown that the catalyst as well as the catalyst distribution influences significantly the electrode reactions and the oxidation mechanism in the electrolyte.

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