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Morphology effects in MgH_2 anode for lithium ion batteries

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ABSTRACT

In order to acquire reproducible electrodes relevant for Li ion batteries new MgH_2 electrodes are successfully obtained from homogenous slurries in N-Methyl-2-Pyrrolidone "NMP" solvent. The electrodes are aimed to elucidate the contribution of the cell components to the electrochemical cycling, in terms of morphology and composition. Various electrode preparations were tested and compared regarding their interaction with Li in a half-cell. The obtained electrochemical cycling curves are discussed according to the ball-milling-induced structural morphology changes and presence of carbon additives, along with the effect of the kinetic rate on the conversion reaction mechanism.

Introduction

Conversion-type anodes are interesting for Li–ion batteries and beyond (Na–ion, Mg and redox flow batteries) as they demonstrate superior capacities and novel chemistries which are different from the well-known intercalation systems [1–7,23]. MgH_2 as anode reacts with 2Li in a conversion reaction, leading to the formation of Mg and precipitation of 2LiH with a high theoretical capacity of 2037 mAh g^{-1} (compared to graphite-anode 372 mAh g^{-1}) and the lowest charge–discharge polarization of any tested conversion-type material [2,8]. These excellent properties indicate that hydride materials could be suitable for applications in the future batteries, such as electrical vehicles. However, a major challenge is the capacity loss after few cycles [8]. It has been reported a beneficial effect of mechanochemical reaction of MgH_2 with Li metal leading to a composite of Mg embedded in a LiH matrix. Starting from the lithiated state, such Mg/2LiH composite has reached a reversible capacity of 1064 mAh g^{-1} during the first cycle [9,10]. However, the poor electronic conductivity of iono-covalent hydrides, such as MgH_2, has to be taken in consideration, in addition to the insulating character of LiH during re-charge. Commercial MgH_2 (particle size 25–100 μm) has shown poor electrochemical activity and practically no discharge capacity. However, even if the particle size is reduced to 0.1–5 μm by ball milling, the agglomeration of the particles into 5–30 μm agglomerates can limit the reversibility of the reactional process [2]. Furthermore, the addition of carbon black has

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been stated helpless since the charge capacity is lost after one discharge. It has also been reported, that the obtained MgH_2 crystallites are in the range of a few nanometers after one cycle [2], which can play a key role in the reduction of the length of the diffusion pathways. On the other hand, the positive volume change of the electrode during the discharge process can influence the conductivity between the particles. Based on lattice parameters, the bulk volume increase from tetra-MgH_2 to 2LiH/Mg is about 85%, such a volume excess is dominated by the presence of the LiH insulator. Thus, the electrode formulation, including shape, morphology and additives, has a large influence on the cycling performance [8,11–13]. However no systematic study has been reported yet regarding the effect of the morphology and cycling conditions of the active material. Hence, more understanding of the mechanistic properties of hydride-based anodes is highly desirable.

Here, we report studies of different MgH_2 anode composite materials which were tape-casted on a Cu current collector using homogenous slurries in *N*-Methyl-2-Pyrrolidone solvent. Various electrode preparations and cycling conditions were used and compared regarding their interaction with Li in a half-cell. The contribution and the nature of the morphology of the MgH_2-based electrodes before and after cycling are presented and discussed, along with some kinetic aspects of the conversion reaction.

Experimental

MgH_2 was purchased from Alfa-Aesar (98% purity). The MgH_2 was ball-milled under argon atmosphere for periods between 0.5 and 24 h using a Fritsch Pulverisette 6 planetary ball-mill with stainless steel vials and balls (ball-to-powder ratio 40:1, rotation speed 350 rpm). The milled MgH_2 powders were ground with carbon black for additional 1 h using Spex 8000 mixer/mill (ball-to-powder 8:1) for improved electronic conductivity. The various samples and their estimated crystallite/particle size are summarized in Table 1. MgH_2 electrodes (~26 μm thick) were obtained from slurries in *N*-Methyl-2-Pyrrolidone solvent (MgH_2/carbon black/Pvdf (Polyvinylidene fluoride) binder, ~7:2:1 by wt. fraction), and the homogenous suspensions were spread out on a copper foil (Cu-dendritic, Battery-grade, Schlenk) before drying over night at 120 °C under dynamic vacuum. The total carbon black contained a mixture of carbon Super-P® (C_{SP}, TIMCAL), specific surface area (SSA) 75 $m^2\ g^{-1}$, and mesoporous carbon (C_{meso}, Sigma–Aldrich) in the weight ratio C_{SP}/C_{meso} 1:1. Two grades of C_{meso} were tested C_{meso1} and C_{meso2}. They have the following morphological characteristics, average particle size/pore size/SSA of 45 μm/10 nm/200 $m^2\ g^{-1}$ and 0.5 μm/14 nm/75 $m^2\ g^{-1}$ for C_{meso1} and C_{meso2}, respectively.

All sample handling was performed in a MBraun glove box under argon atmosphere (H_2O and $O_2 < 0.1$ ppm). The liquid electrolyte 1M $LiPF_6$ in 1:1 ethylene carbonate/diethylene carbonate (LP30, BASF) was used without any additional additives and showed no reaction with the hydride. A homemade "ETH-cell" battery cell consisting of a stainless-steel outer casing and inner parts in titanium was used for cycling. The cell was loaded with the active material in the glovebox, then covered by a separator layer (Whatman®) soaked in 80 μl of the selected electrolyte, before the lithium foil was placed on top. The assembled cells were cycled in galvanostatic mode at 30 °C between 0.2 and 2.5 V vs. Li^+/Li redox couple (C-rate C/20) using an Arbin Battery cycler (Arbin Instruments). The electrochemical capacity is reported per mass unit (g) of the MgH_2 active material. The lithiation of carbon black is expected to be small and similar for all samples [11] and its contribution was neglected. The voltage cutoff at 0.2 V was applied for all the cells so that to avoid the formation of the hcp Mg-type and bcc Li-type solid solutions at lower voltage [2,13].

Synchrotron radiation powder X-ray diffraction (SR-PXD) patterns were obtained at the Swiss-Norwegian Beamlines (SNBL, BM01), ESRF, Grenoble with a Pilatus2M 2-dimensional detector and a wavelength of 0.77787 Å. The samples were contained in 0.5 mm boronglass capillaries that were rotated 90° during the 30 s exposure. The sample-detector distance was 345.97 mm 1D data were obtained by integration of the 2D diffraction patterns with the program Bubble [14]. Crystallite size was obtained with the Scherrer equation from the positions and FWHM (Full Width at Half Maximum) of the diffraction peaks. The broadness of the Bragg peaks was corrected for the instrumental contribution using LaB_6 standard. The microstrain contribution to the broadening was disregarded as it remains at a minimum level even after long-time milling of MgH_2 [15]. Scanning electron microscopy (SEM) was performed using a Hitachi S-4800. Focused ion beam-scanning electron microscopy (FIB-SEM) was carried out with a FEI Helios 600 dualBeam FIB. The Ga^+ ion beam was used to cut down through the electrode for cross-section imaging. TEM was performed with a double Cs corrected JEOL coldFEG ARM200CF, operated at 200 kV.

Table 1 – Samples, milling times, estimated crystallite size (XRD) and particle size range (SEM/TEM).

Designation	Milling time, h	Crystallite size, nm	Particle size, μm
As-received	0	97 ± 18	25–100
MgH_2-A	½	18 ± 3	<5
MgH_2-B	2½	10 ± 2	<1
MgH_2-C	5	8 ± 1	0.1–0.4
MgH_2-D	10	7 ± 1	0.05–0.3
MgH_2-E	24	7 ± 1	0.05–0.2

Results and discussion

Materials characterization

Fig. 1 shows the SR-PXD patterns of MgH_2 milled at different times as well as the as-received material. For the as-received powder, all Bragg peaks correspond to *tetra*-MgH_2 phase with very small amounts of Mg. By milling, it can be noticed a significant increase of the intensity of the Mg reflections and the appearance of the metastable *ortho*-MgH_2 phase after ½ h of milling. This latter phase has been shown to form in minor amounts from *tetra*-MgH_2 during milling [16–18] and under