Reversibility of metal-hydride anodes in all-solid-state lithium secondary battery operating at room temperature

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ABSTRACT

The impact on the performance of conversion-type MgH_2 anodes by using solid state electrolyte is reported. MgH_2 anodes (~26 μm thick) made from homogenous slurries and subsequent drying, are used as model systems along with $Li(BH_4)_{0.75}I_{0.25}$–$0.8Li_2S·0.2P_2S_5$ as solid electrolyte in an "all-solid-state room-temperature secondary battery". Electrochemical tests are carried out to investigate cycling properties and elucidate reversibility aspects during the conversion reaction. A major enhancement in performance is observed for the all-solid-state battery compared to MgH_2 anodes using carbonate-based liquid electrolytes. This shows that good compatibility and improved reversibility can be obtained for hydride anodes when associated with borohydride-based electrolyte in a Li-ion cell operating at room temperature.

1. Introduction

Conversion-type anodes are interesting for Li-ion batteries owing to their specific mechanistic properties and high capacity compared to conventional insertion-type anodes such as graphite. Hydride based anodes, for example MgH_2, have been demonstrated for Li-ion batteries [1,2]. MgH_2 reacts with 2Li in a chemical reaction (redox potential 0.45 V vs. Li^+/Li), leading to the formation of 2LiH and Mg and thus allowing a storage capacity of about $2\,Ah\,g^{-1}$ with low polarization during the discharge-charge processes [1,3,4]. Besides, these materials have the peculiarity to cover the weaknesses of oxide based conversion-type anodes in which the high working potential and large (de)lithiation cycling hysteresis hinder its quick application in Li-ion batteries [5]. On the other hand, the application of hydride anodes is still a challenge owing to capacity loss after several cycles, starting either from the charged or discharged states [2,3]. The bulk volume variation between these two states, i.e. tetra-MgH_2 and 2LiH/Mg, is about 83% which can influence the electron conductivity between the particles [6]. The reported electrochemical tests using MgH_2 show only a partial reversibility at room temperature (RT), either using liquid or solid electrolytes [1,3,7–9]. A reversible capacity of ca. 75% is reached for a liquid electrolyte during the first cycle [2,3,6]. However, in solid state using the glass system Li_2S-P_2S_5, Ikeda et al. [7] reported around 31% reversible capacity at RT. Possible interaction with the solid electrolyte (SE) at the electrode/electrolyte interface was pointed out. Better

performance has been reached using $LiBH_4$ as SE at higher temperatures at 120 °C [10–12], or $Li(BH_4)_{0.75}I_{0.25}$ at 150 °C [13]. Considering formulation effects (morphology, additives and coating) which may influence the cycling performance [14–17], an optimization of the design of the electrode is required before any cell with a suitable choice of SE can be made.

Here, we report our recent findings on the reversibility of MgH_2 anodes at RT when embedded in a SE for tests in a Li-ion cell configuration. A new electrolyte with reasonable ionic conductivities has been synthesized; Li_2S-P_2S_5 is stabilized by adding $Li(BH_4)_{0.75}I_{0.25}$ followed by annealing. The presence of SE at RT removes most issues connected with SEI-like degradations, even though some other interfacial aspects appear according to the existence of path dependence in this electrode. The obtained experimental results are presented and discussed in relation to previous analytical works [16].

2. Experimental

MgH_2 was purchased from Alpha-Aesar (98% purity). The MgH_2 powders were ball-milled (24 h) under hydrogen atmosphere (5 MPa) using planetary ball-mill with stainless steel vials and balls (ball-to-powder ratio 40:1, 400 rpm). $LiBH_4$ (95%), LiI (99.9%), Li_2S (99.98%) and P_2S_5 (99%) were purchased from Sigma-Aldrich. The halide-stabilized hexagonal phase $Li(BH_4)_{0.75}I_{0.25}$ was synthesized according to the procedure described by Miyazaki et al. [18]. The amorphous precursor

0.8Li$_2$S·0.2P$_2$S$_5$ was prepared by ball-milling for 20 h using planetary ball-mill (ball-to-powder ratio 40:1, 370 rpm) [19,20].

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 or 0.6973 Å. The samples were contained in 0.5 mm borosilicate capillaries that were rotated 90° during 30 s exposure. The sample - detector distance was 345.97 mm. 1D data were obtained by integration of the 2D diffraction patterns using the program Bubble [21]. Crystallite sizes were determined with the Scherrer equation from the FWHM (Full Width at Half Maximum) of the diffraction peaks, corrected for instrumental broadening using LaB$_6$ as standard. The microstrain contribution to the broadening was disregarded as it remains at a minimum level after long-time milling [22]. TEM was performed with a double Cs corrected JEOL coldFEG ARM200CF, operated at 200 kV. Focused ion beam – scanning electron microsocopy (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.

The ionic conductivity of the solid electrolytes was investigated by Electrochemical Impedance Spectroscopy (EIS) measurements using a Novocontrol Alpha-A frequency analyzer (Montabaur, Germany). The as-milled materials were first pressed into pellets with a diameter of 8 mm and thicknesses from 0.6 to 0.9 mm by using a uniaxial press at around 550 MPa. The pellets were sandwiched between lithium foils as non-blocking electrodes, and sealed in a stainless steel cell. Temperature-dependent measurements were performed in Ar using a Probostat (NorECs AS) sample holder from *RT* up to 120 °C. Measured impedance spectra were analyzed by equivalent circuits using ZView2 software (Scribner Associates Inc.). Total conductivity was calculated using the resistance obtained from data fitting and the sample geometry.

All-solid-state battery cells were prepared in coin cell configuration using standard TiS$_2$ and MgH$_2$ as active electrodes, respectively. For the cell with TiS$_2$, the TiS$_2$ (99.9%, Sigma-Aldrich) powders and the prepared SE powders were weighed in a 2:3 mass ratio and manually mixed by an agate mortar/pestle. The obtained mixture was used as the electrode composite. About 6 mg of this composite and 50 mg of the SE were introduced in a 10 mm die set and pressed together uniaxially at 240 MPa. A Li foil was placed on the opposite side of the material composite as counter/reference electrode. The resulted multi-layer pellet was inserted in a CR2032 coin cell. To ensure thinner electrodes and to better optimize the diffusion pathways, thin electrode tapes (26 µm) containing MgH$_2$ were prepared and adhered on the dendrite surface of the Cu foil [16]. The final electrodes were cold pressed with the SE and lithium foil at 240 MPa. The following cells were then assembled:

Battery 1: TiS$_2$/SE | SE | Li

Battery 2: MgH$_2$ − tape | SE | Li

All handling was performed in a MBraun® glove box under Ar atmosphere (H$_2$O and O$_2$ < 0.1 ppm). A home-made "ETH-cell" battery cell consisting of a stainless-steel outer casing and inner parts in titanium was used for cycling. The cells were cycled at 30 °C (0.01 mA cm^{-2}) in the potential range 1.6–2.7 V for TiS$_2$ and 0.2–2 V for MgH$_2$, respectively, using an Arbin Battery cycler (Arbin Instruments®). The voltage cut-off at 0.2 V was applied to avoid formation of Mg−Li solid solutions at lower voltage [1,6].

3. Results and discussion

3.1. Materials characterization and properties

Microstructural characteristics (SR-PXD) of the MgH$_2$ powder, as seen in Fig. 1, indicate a well crystalline *tetra*-MgH$_2$ with significant
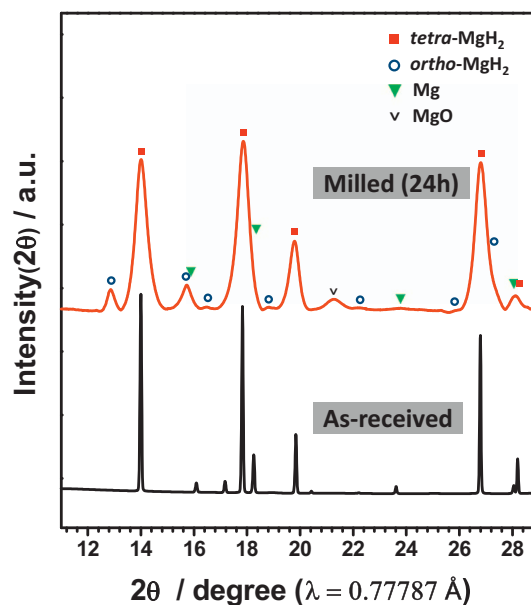

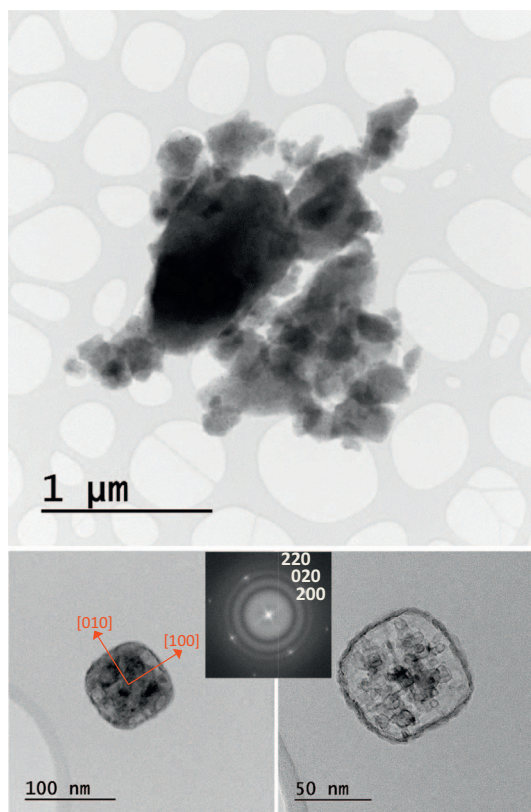**Fig. 1.** SR-PXD patterns of the 24 h–milled MgH$_2$ under H$_2$ atmosphere 5 MPa.

Fig. 2. Bright field TEM micrographs of the 24 h–milled MgH$_2$ under H$_2$ atmosphere 5 MPa: Overview picture (top) and higher magnification on one single particle (bottom). Inset: Fourier transform of the bright field TEM image.

presence of elemental Mg. Subsequent milling leads to reduced grain size (3–7 nm), given the broadening of the Bragg peaks. The microstrain is assumed to be negligible and < 0.1% [16]. The milled material shows no or very little presence of Mg, presumably due to hydrogenation during the milling process. In accordance with previous works, significant amounts of metastable *ortho*-MgH$_2$ is formed and depends on the milling conditions [16]. However, it is not clear whether the formation of *ortho*-MgH$_2$ occurs during hydrogenation of the Mg impurity