



Electrochemical properties of $\text{MgH}_2 - \text{TiH}_2$ nanocomposite as active materials for all-solid-state lithium batteries

Anh Ha Dao^{a,b}, Nicola Berti^b, Pedro López-Aranguren^{a,*}, Junxian Zhang^b, Fermín Cuevas^b, Christian Jordy^a, Michel Latroche^b

^a Saft, 111 boulevard Alfred Daney, 33074 Bordeaux Cedex, France

^b Université Paris Est, ICMPE (UMR7182), CNRS, UPEC, F-94320 Thiais, France



HIGHLIGHTS

- $x\text{MgH}_2 + (1-x)\text{TiH}_2$ nanocomposites are integrated in Li-ion solid-state battery.
- The conversion reaction with Li is studied in the composition range $0.2 \leq x \leq 0.8$
- Mg-rich composites exhibit excellent reversible capacity: 1700 mAh g^{-1} for $x = 0.7$
- Ti-rich composites ($x = 0.2$) have a good capacity retention over 10 cycles.

ARTICLE INFO

Keywords:

Metal hydrides
All-solid-state batteries
Lithium borohydride

ABSTRACT

This study reports on solid-state batteries operating at 120°C prepared with metal hydride *MH* nanocomposites $x\text{MgH}_2 + (1-x)\text{TiH}_2$ used as active materials for the positive electrode, metallic Li as the negative electrode and LiBH_4 as the solid electrolyte. The molar content x of the *MH* nanocomposites ranged from 0.2 to 0.8. The electrochemical properties of the metal hydride electrodes are here scrutinized as a function of the chemical composition of the active materials. Mg-rich nanocomposites offer higher specific capacity (over 1700 mAh g^{-1} at C/50 regime for $x = 0.7$), whereas Ti-rich ones exhibit better cycle-life (ca. 100% capacity retention after 10 cycles for $x = 0.2$). In comparison to equivalent liquid electrolyte cells operated at RT, solid-state cells show improved properties such as a coulombic efficiency above 98% and a rate capability of ca. 50% of delivered capacity at 1C-rate. It is also evidenced that mass transport within the working electrode is a key factor limiting the reversibility of hydride conversion reactions. This work represents a deep insight on the hurdles of metal hydrides to be used as efficient anode materials for Li-ion batteries.

1. Introduction

The increasing worldwide demand of clean energy systems leads scientists to develop new efficient means for energy conversion and storage. In this context, electrochemical storage has become nowadays the most common way to handle renewable energy resources and to power electric vehicles and electronic devices. Lithium ion batteries (LiBs) are foreseen as a promising electrochemical technology to meet the as-mentioned high-energy requirements. In the last ten years, graphite has been used as negative electrode for commercial LiBs, with a limited specific capacity of $370 \text{ mAh}\cdot\text{g}^{-1}$ [1]. To increase the current specific energy of LiBs, researchers are addressing their efforts to develop new materials with enhanced capacity. Metals or semimetals such

as aluminum, tin and silicon are attractive candidates because of their large capacity through alloying-type reactions, e.g. over 3600 mAh g^{-1} for $\text{Li}_{15}\text{Si}_4$ alloy [2,3]. However, the large volume changes occurring during reversible lithiation leads to loss of electrical contact, limiting their cycle-life. This issue has been largely solved by nanostructuring and composite formation. For instance, Si-C nanocomposites show capacity exceeding 1000 mAh g^{-1} for more than 200 cycles [4]. Alternatively, through a conversion reaction scheme, nanostructured materials based on transition metal oxides have been demonstrated to be promising anodes [5]. Fe_2O_3 -based materials can deliver a reversible capacity of 800 mAh g^{-1} , with working potential of $\sim 1.0 \text{ V}$ (vs Li/Li^+) [6]. Irreversibility of the conversion reaction and volume expansion concerns in these materials have been successfully improved [1,7].

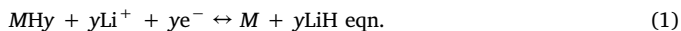
* Corresponding author. CIC Energigune, C/Albert Einstein, 48, 01510, Miñano, Alava, Spain.

E-mail addresses: dao-ha@icmpe.cnrs.fr (A.H. Dao), berti@icmpe.cnrs.fr (N. Berti), plopez@cicenergigune.com (P. López-Aranguren), junxian@icmpe.cnrs.fr (J. Zhang), cuevas@icmpe.cnrs.fr (F. Cuevas), Christian.JORDY@saftbatteries.com (C. Jordy), latroche@icmpe.cnrs.fr (M. Latroche).

<https://doi.org/10.1016/j.jpowsour.2018.07.028>

Received 18 March 2018; Received in revised form 2 July 2018; Accepted 4 July 2018
0378-7753/ © 2018 Published by Elsevier B.V.

However, metal oxides face, as intrinsic issue, a large voltage hysteresis (*i.e.* polarization) observed between discharge and charge, which severely diminishes the round-trip efficiency of the electrode. In 2008, metal hydrides (MH_y) were proposed as high capacity anode materials for LiBs [8]. The conversion reaction for metal hydrides is written as:



Metal hydrides such as MgH_2 and TiH_2 with $y = 2$ can provide theoretical specific capacities of 2038 and 1074 mAh g^{-1} , with low working potentials of 0.55 and 0.22 V vs. Li/Li^+ , respectively and low polarization. The properties of negative electrodes for LiBs based on MgH_2 and TiH_2 have been already reported in previous works [9–13], with successful electrochemical behavior in solid-state batteries (SSBs) using $LiBH_4$ as solid electrolyte (SE) [14,15]. These batteries were operated at 120 °C, for which the ionic conductivity of SE $LiBH_4$, $\sigma = 10^{-3} \text{ S cm}^{-1}$, approaches that of conventional liquid electrolytes [16,17]. In a previous publication, we built for the first time a complete SSB metal hydride – sulfur Li-ion cell. We evidenced the excellent compatibility of this redox couple and its outstanding electrochemical performance [18]. An interesting approach to enhance the individual properties of the two hydrides MgH_2 and TiH_2 is to combine them to form a nanocomposite. The addition of TiH_2 to MgH_2 improves the MgH_2 electrochemical behavior, electronic conductivity, and hydrogen transport [11,19]. Thus, the electrochemical performance of a $0.7MgH_2 + 0.3TiH_2$ composite using an organic liquid electrolyte has been reported by Huang et al. [11]. Kinetics of the MgH_2 conversion reaction are enhanced as well as the reversibility at room temperature (RT) of the conversion of TiH_2 with lithium, which is not observed when using TiH_2 alone. Moreover, Berti et al. [20] have recently shown that the cooperative effect between MgH_2 and TiH_2 can be tuned by adjusting the molar ratio of the hydrides. Indeed, the reversibility of the conversion reaction at RT increases with the quantity of MgH_2 into the composite. On the basis of these results, we have prepared a set of nanocomposites $xMgH_2 + (1-x)TiH_2$ with molar ratio $x = 0.2, 0.5, 0.7,$ and 0.8 . Molar contents close to single phase hydrides, such as $x = 0.1$ and 0.9 , have been discarded from this study to promote significant synergetic effects between the two hydride phases. These composites have been used for the preparation of positive electrodes to assembly all-solid-state batteries using $LiBH_4$ as solid electrolyte and lithium as negative electrode. The aim of this work is to provide a systematic study of the electrochemical performance of the nanocomposites as a function of molar ratio x to clarify synergetic effects between MgH_2 and TiH_2 in a solid-state cell. For this purpose, voltage profiles, capacity retention and rate capability have been obtained from galvanostatic cycling measurements. Impedance spectra have been collected during the redox steps to evaluate evolution of the resistance of the all-solid-state cell.

2. Experimental

2.1. Preparation of the cathode composites and the all-solid-state half-cells

A range of molar compositions $xMgH_2 + (1-x)TiH_2$ with $x = 0.2, 0.5, 0.7,$ and 0.8 was prepared from powders of Mg (Alfa Aesar, 99.8%, 140–800 μm) and Ti (Alfa Aesar, 99.9%, 100 μm). The synthesis and nanostructuring of the composite was obtained by reactive ball milling (RBM) under hydrogen pressure. Powders of Mg and Ti were loaded in a 220 cm^3 jar with 40 stainless-steel balls of 12 mm in diameter. The ball-to-powder mass ratio (BPR) was set to 60: 1. Next, the jar was filled with 9 MPa of H_2 (6 N Alphagaz) and then placed in a planetary mill (Fritsch Pulverisette 4). The powders were milled during 4 h applying a middle pause of 2 h to avoid overheating of the system. The rotation speed of the vial and disk were fixed to 400 and -400 rpm, respectively. The final electrode was prepared by ball milling of the MH nanocomposite with $LiBH_4$ (Rockwood Lithium GmbH, $\geq 95\%$) and carbon Timal SUPER C65 (denoted hereafter as C65). The targeted

electrode composition MH: $LiBH_4$:C65 was 30:50:20 (wt. %). The three components with an overall mass of 0.5 g were milled under argon atmosphere for 2 h at a milling speed of 300 rpm and BPR of 40:1. For this purpose, a planetary mill (Frisch Pulverisette 5) was used. Five minute rest intervals were fixed between 15 min rest periods. The half-cells were assembled with the following configuration: MH/ $LiBH_4$ /C65 | $LiBH_4$ | Li by pelletizing the powders with a 10 mm diameter stainless-steel die (Specac). First, ca. 3 mg of the electrode material were pressed at 0.2 tons, then, 30 mg of $LiBH_4$ powder was added and the whole was pressed at 2 tons to obtain a cathode/electrolyte bilayer pellet. To complete the cell assembly, a Li foil disk (200 μm) of 9 mm diameter was added on top of the solid electrolyte to serve as anode. For the electrochemical measurements, all the cells were enclosed in a homemade sealed Teflon Swagelok cell shown elsewhere [18].

2.2. Characterization of the MH nanocomposites by X-Ray power diffraction

The structural properties of the MH nanocomposites were investigated by X-Ray Powder Diffraction (XRD, Bruker D8 Advance) using $Cu-K_{\alpha 1,2}$ radiation. To avoid air contamination, all XRD analysis were performed under argon atmosphere with the help of a specially designed airtight sample holder.

2.3. Microstructural characterization of the electrodes

To get information on the spatial distribution of the hydride phases within the powder nanocomposite, TEM analysis was performed using a 200 kV FEG TEM device (FEI Tecnai F20). The composite was immersed in dimethyl carbonate (DMC) and placed over a carbon grid. The spatial phase distribution was analyzed by image acquisition in High-Angle Annular Dark Field (HAADF) mode. Morphological and chemical examination of as-milled MH/ $LiBH_4$ /C65 electrodes were conducted with a high-resolution FEG SEM equipped with EDX microanalysis. As-milled powders were attached to a sticky carbon tape, and SEM images were acquired in secondary electron mode.

2.4. Electrochemical characterization

Prior to the electrochemical measurements, all cells were annealed at 120 °C during 5 h. Discharge/charge cycling profiles were obtained using a multichannel battery tester (MPG-2, Biologic). AC impedance measurements of the half-cells were obtained using an Autolab PGSTAT30 potentiostat, setting an input voltage perturbation and a frequency rate of 10 mV and 1 MHz–1 Hz, respectively. All the measurements were carried out in a furnace at 120 °C. Impedance spectra were fitted by using EC-Lab software.

3. Results and discussion

3.1. Characterization of hydride nanocomposites

The XRD patterns of $xMgH_2 + (1-x)TiH_2$ composites with $x = 0.2, 0.5, 0.7$ and 0.8 obtained by RBM are shown in Fig. 1.

Diffraction peaks for compositions $x = 0.8$ and 0.7 were assigned to the co-existence of γ - MgH_2 , β - MgH_2 and ϵ - TiH_2 , in agreement with the literature [20]. Peaks corresponding to γ - MgH_2 could not be detected for $x = 0.5$, neither those related to any MgH_2 phase for $x = 0.2$. This is related to the lower amount of such MgH_2 phases and weak diffraction power of Mg vs Ti in these compounds. All hydride powders consist of micrometric size agglomerates formed by primary particles with an average crystallite size in the range 4–11 nm (Table S1 in the ESI), as determined from the broadening of the XRD lines using the Scherrer formula and considering the instrumental resolution. TEM images (Fig. S1 in ESI) illustrate the presence of two phases, MgH_2 and TiH_2 , intimately mixed together at the nanoscale in all composites.

Download English Version:

<https://daneshyari.com/en/article/7724762>

Download Persian Version:

<https://daneshyari.com/article/7724762>

[Daneshyari.com](https://daneshyari.com)