



Thin films as model system for understanding the electrochemical reaction mechanisms in conversion reaction of MgH_2 with lithium

N. Berti^a, E. Hadjixenophontos^b, F. Cuevas^{a,*}, J. Zhang^a, A. Lacoste^c, P. Dubot^a, G. Schmitz^b, M. Latroche^a

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

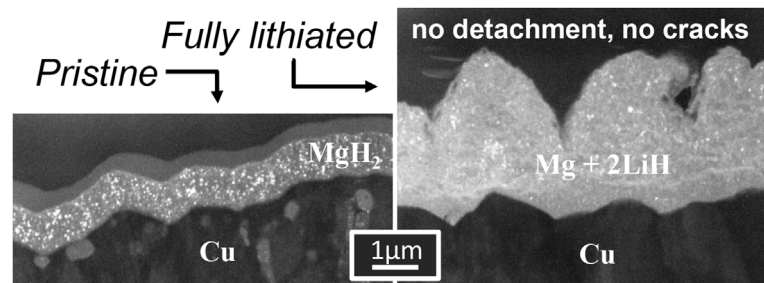
^b Institut für Materialwissenschaft, Lehrstuhl Materialphysik (IMW), University of Stuttgart, Heisenbergstrasse 3, Stuttgart, 70569, Germany

^c LPSC, Université Grenoble-Alpes, CNRS/IN2P3, 53 rue des Martyrs, Grenoble Cedex, 38026, France

HIGHLIGHTS

- Conversion reaction of MgH_2 with Li studied for $1\ \mu\text{m}$ thin films.
- Al-coating diminishes surface MgO formation and allows full lithiation of MgH_2 .
- No electronic degradation during first cycle, but reversibility limited to 25%.
- Reversibility issues of hydrides at RT assigned to mass-transport limitations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Metal hydride
Li-ion batteries
Conversion reaction
Magnesium hydride
Thin film
Transmission electron microscopy

ABSTRACT

Metal hydrides are promising high-capacity anode materials for Li-ion batteries but their conversion reaction with lithium suffers from low reversibility at room temperature (RT). Irreversibility issues in magnesium hydride MgH_2 thin films are investigated, as well-defined model system. Films are deposited over Cu current collectors by means of microwave plasma-assisted sputtering and coated with aluminum to minimize formation of passivating MgO native oxide. Structural and chemical properties of the electrodes have been analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and electrochemical impedance spectroscopy (EIS). Galvanostatic cycling reversibility at RT and C/50 regime is limited to 25% in the first cycle for $1\ \mu\text{m}$ thick films. The lithiation of the thin film is complete and doubles its thickness. Despite drastic volume changes, neither cracks, voids, nor detachment of the thin film from the substrate are noticed. Moreover, electronic resistivity decreases upon lithiation due to the formation of metallic Mg. The origin of irreversibility phenomena in MgH_2 films is attributed to sluggish mass transport of species within the electrode at RT.

1. Introduction

Developing a new generation of Li-ion batteries with higher energy density is an urgent demand due to the expansion of portable devices as

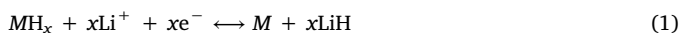
well as electric vehicle markets. A critical issue to develop high capacity battery is the replacement of graphite as negative electrode. During the 90's, graphite was chosen as anode because of its stability, safety, and long cycle-life. However, the intercalation of lithium ions within the

* Corresponding author.

E-mail address: cuevas@icmpe.cnrs.fr (F. Cuevas).

graphite planes is limited to 1 Li atom for 6 C atoms, providing a theoretical capacity of 372 mAh g^{-1} . To satisfy the energy density demand, new materials that react with lithium achieving higher capacities are needed. Thus, novel reaction schemes based on alloying or conversion mechanisms have been proposed [1]. Among the conversion electrode materials reported in literature, such as oxides, fluorides, nitrides, sulphides, and phosphides [2,3], metal hydrides [4] have been also suggested as possible candidates as negative materials.

Metal hydrides react with lithium ions at potentials below 1 V vs. Li/Li⁺ according to the general conversion reaction:



where the amount of reacting Li atoms x equals to the hydrogen content of the metal hydride. Many metal hydrides provide capacities in the order of thousands of mAh g^{-1} [5], making them promising candidates as negative electrodes in Li-ion batteries. However, metal hydrides are still far from practical application due to their poor reversibility and short cycle-life. MgH_2 was the first hydride investigated as electrode material. During the conversion reaction, magnesium hydride is reduced to metallic Mg and hydride LiH. This reaction occurs at an average voltage of 0.55 V vs. Li/Li⁺, providing a theoretical capacity of 2036 mAh g^{-1} for $x = 2$, almost six times that of graphite. However, as shown by Brutti et al. [6], the capacity of MgH_2 quickly fades during the first 3–4 cycles. Different strategies have been suggested with the purpose of enhancing the performance of MgH_2 electrode. For instance, Oumellal et al. [4] achieved a good capacity retention limiting the conversion reaction to $x = 0.5$ Li, with the electrode delivering about 500 mAh g^{-1} after 50 cycles. Similar capacity was obtained by nanoconfining MgH_2 particles into a porous carbon scaffold [7]. Moreover, Zaidi et al. [8] suggested the use of carboxymethyl cellulose as binder in order to accommodate the volume changes during discharge/charge cycling. This provided a relatively stable capacity of $\sim 600 \text{ mAh g}^{-1}$ after 40 cycles.

Despite these improvements, the capacity provided by MgH_2 is still far from its theoretical value. Previous authors [5,6,9,10] have tried to explain this poor reversibility emphasizing the fact that volume changes during cycling might lead to cracks and loss in contact between particles, limiting the extent of the conversion reaction due to electrical disconnection. Furthermore, the formation of insulating LiH could also hinder electronic conductivity within the electrode. Beside electronic issues, the conversion reaction entails a complex solid-solid reaction mechanism that involves hydride decomposition, displacement between Li and H atoms as well as phase nucleation and growth. Thus, the completion of the conversion reaction requires fast enough mass transport of atomic species at room temperature (RT). Nevertheless, clear evidences of which phenomena are the main issues of the poor reversibility and short cycle-life are still lacking in literature.

Hereby, we systematically investigate the structural and chemical properties of MgH_2 thin film electrode step by step during the reaction with lithium. Thanks to their well-defined 2D morphology, thin films are ideal systems to study the effect of the conversion reaction on the electrode morphology. Moreover, with the help of microscopy imaging analysis, the mechanism and spatial localization of the different phases can be determined within the electrode. The purpose of this work is to better describe the path of the conversion reaction trying to highlight chemical, structural and morphological changes within the film and its impact on the reversibility of MgH_2 electrode.

2. Experimental

Magnesium hydride thin films, about $1 \mu\text{m}$ in thickness, were prepared by microwave plasma-assisted sputtering [11] over rough Cu current collectors $16 \mu\text{m}$ in thickness (SAFT, France). The surface roughness R_z is $0.5 \mu\text{m}$. Films were prepared either in bare state or coated with an Al over-layer (Al– MgH_2). In the deposition chamber a

Ar– H_2 mixture plasma is generated at very low pressure (0.2 Pa of partial pressure for both gasses) by means of a set of multi-dipolar microwave couplers. Magnesium atoms are sputtered by Ar ions from metal targets (99.99% Mg) and directed towards the copper substrate (square shaped $6.7 \times 6.7 \text{ cm}$) where they ultimately condense and react with hydrogen forming MgH_2 . Film growth rate was 15 nm/min . During the deposition, the temperature of the substrate (water cooled) did not exceed $30 \text{ }^\circ\text{C}$, avoiding any thermal-driven reaction between the deposit material and the substrate. For the Al-covered thin films, after the formation of hydride MgH_2 , Al metal was deposited at a rate of 6.5 nm/min for 2 min ($13 \text{ nm Al-thickness}$) on top of the films under 0.2 Pa of argon atmosphere. Al-coating aimed to preventing contamination of MgH_2 when films were exposed to air after their preparation. Aluminum was chosen as protective material because as a metal it shows reactivity towards lithium [12,13], allowing the Li ions to diffuse and reach the hydride below. Moreover, the expected formation of native oxide Al_2O_3 upon air-exposure has shown to improve the rate capability of different materials for Li-ion batteries [14,15].

Structural properties of the thin films were investigated by X-ray diffraction (XRD) using a D8 Advance Bruker diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). An especially design air-tight sample-holder was used to perform XRD under argon atmosphere to avoid contamination during the measurements. Surface analyses were carried out by X-ray photoelectron spectroscopy (XPS) in the system Thermo VG Scientific K-alpha, with monochromatic Al-K α X-ray source ($h\nu = 1486.7 \text{ eV}$). Microstructural investigations of the thin films were performed by transmission electron microscopy (TEM) using a PHILIPS CM200, performing selected area electron diffraction (SAED) at 200 kV . To allow the use of TEM, small lamellas were prepared from the thin films by focused ion beam (FIB) using a SCIOS-FEI dual beam FIB/SEM. Prior to the cross sectioning, a layer of $\sim 2 \mu\text{m}$ of platinum was deposited on top of the thin film to protect the area of interest from the Ga-ion beam. Next, the thin film is excavated around the selected area, creating a thin lamella. The width of the lamella, *i.e.* the thickness through which TEM radiation should pass perpendicularly to the cross section, is less than 100 nm .

For electrochemical studies, a square of 9 mm side of thin film was cut and placed in a Swagelok cell as working electrode. It was separated from the counter electrode, lithium foil (9 mm diameter disk), by two Whatman glass fiber filters imbued with liquid electrolyte 1.0 M LiPF_6 (in 1:1wt. DMC:EC). Electrochemical analyses were carried out using a Bio-Logic VMP3 multichannel potentiostat. Galvanostatic discharge/charge cycling of the half-cells was performed at a rate of one equivalent lithium in 25 h. This corresponds to the lithiation/delithiation of the metal hydride at a regime of $C/50$. Electrochemical impedance spectroscopy (EIS) was performed on half-cell in the frequency range between 0.1 Hz and 1 MHz , with a perturbation current of $50 \mu\text{A}$.

3. Results

3.1. Thin film characterization

Thin film morphology was analyzed by FIB-SEM (Figure S1 in supporting information SI) for the uncovered sample. The thickness of MgH_2 film is *ca.* $1 \mu\text{m}$. It was evenly deposited over the rough Cu substrate. The film growth was conformal without voids leading to a surface topography analogous to the pristine Cu substrate. XRD patterns of bare MgH_2 and Al– MgH_2 thin films show two phases (Fig. S2): tetragonal rutile-type $\beta\text{-MgH}_2$ with S.G. $P4_2/mnm$ and *fcc* Cu with S.G. $Fm\bar{3}m$. For the Al– MgH_2 thin film, no peaks related to the aluminum coating could be found, likely due to its small amount.

The surface composition of both bare and Al-covered MgH_2 has been analyzed by XPS. The spectra are displayed in Fig. 1 for photoelectron Al 2p peaks (Fig. 1a) and Auger Mg $\text{KL}_{2,3}\text{L}_{2,3}$ peaks (Fig. 1b). XPS spectra in the Al 2p region (Fig. 1a) evidence the occurrence of an oxidized aluminum thin film for the coated sample, whereas no signal is

Download English Version:

<https://daneshyari.com/en/article/10154684>

Download Persian Version:

<https://daneshyari.com/article/10154684>

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