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H₂ thermal desorption and hydride conversion reactions in Li cells of TiH₂/C amorphous nanocomposites

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ABSTRACT

Here we investigate the properties of amorphous TiH₂/carbon nanocomposites as possible active material in lithium cells. Several TiH₂/C mixtures are prepared by a mechanochemical route, by varying the carbon/hydride ratio. Materials are tested in electrochemical cells versus lithium metal in EC:DMC LiPF₆ electrolyte by galvanostatic cycling (GC) and are characterized by X-ray diffraction, transmission electron microscopy, thermogravimetry and mass spectrometry. Thermal dehydrogenation processes are altered by the mechanochemical treatment of the sample: milling decreases the hydrogen content of the hydride. On the other hand, the mechanochemical grinding increases the specific capacity delivered during the first GC discharge. We suggest that the electrochemical process is the result of a delicate balance between the absolute quantity of hydrogen and its availability for the hydride conversion reaction.

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1. Introduction

Portable electronic devices are actually powered by lithium ion batteries and their market is rapidly expanding. However Li-ion batteries currently suffer of both safety and performance limits which hinder their use for high current application (e.g. hybrid or electric vehicles). To overcome these restrictions new negative electrode materials are under investigation [1–3]. Among them, metal hydrides may theoretically operate in a rechargeable lithium cell through a conversion process (hydride conversion reaction, HCR) according to the scheme: $M_xM'_yH_z + z e^- + zLi^+ = M_xM'_y + zLiH$, where e^- and Li^+ are the electron and the lithium ion, respectively [4]. In the HCRs the metal hydride gives hydrogen atoms to Li, forming metal nanoparticles surrounded by LiH; these processes are theoretically capable to disclose outstanding improvement in the negative electrode specific capacity [5]. Only few studies describe HCR processes, mainly for MgH₂ [4–6]. Recently TiH₂ has been investigated by Oumellal and coworkers [7] because it has large theoretical weight and volumetric capacities, i.e. 1074 mA h g⁻¹ and 3815 mA h l⁻¹, respectively.

Here we report on the use of amorphous TiH₂/carbon nanocomposites as active material in lithium cells. Several TiH₂/C

composites have been prepared by means of a mechanochemical route by varying the carbon/hydride ratio. A comparison between the dehydrogenation processes induced by the thermal treatments and the HCR reaction steps in lithium batteries is here sketched for the first time.

2. Materials and methods

The pristine TiH₂ powder has been purchased from Sigma–Aldrich Co. (98% purity) and has been used without further purification. All the handling procedures of samples have carried out in argon-filled glove boxes. Samples have been prepared by using a high energy shaker, Retsch mm400. A stainless steel jar have been filled with 400 mg of powder and a single 4 g stainless steel ball (1 cm diameter); the speed has been set at 25 Hz. The three samples studied are:

Sample A – TiH₂ pristine material.

Sample B1 – TiH₂ powder ball milled for 1 h.

Sample B1D1 – TiH₂ powder ball milled for 1 h and then ball milled 1 h with Super P carbon (Timcal) in a ratio of 5:3.

X-ray diffraction on sealed glass capillaries has been used to verify the samples crystallinity by using a Rigaku Ultima+ diffractometer. Transmission electron microscopies have been recorded by using a FEI Tecnai 200 kV instrument.

Simultaneous TGA–DSC experiments have been performed using a Setaram Set-sys Evolution 1200 TGA System. After purging the TGA oven, the system has been flooded with high purity argon and measurements have been performed with a gas flow of 40 ml/min. Concomitant MS analysis of the released gas has been carried out by a calibrated Pfeiffer Prisma analyzer (QMS200). Electrodes for electrochemical tests have been produced in an Ar-filled glove box (MBraun, water and O₂ content below 1 ppm) as pellets supported on thin copper films by cold pressing

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a hand grinded mixture of TiH_2 , Super P and polyvinylidene fluoride (PVdF Kynar 2801, Atochem) in weight ratio 5:3:2. Lithium cells have been assembled using LP30 Merck electrolyte (LiPF_6 1 M in ethylene carbonate dimethyl carbonate 1:1 mixture) and a lithium foil as counter electrode. Discharge–charge galvanostatic cycling (GC) has been carried out at a C/100 current density (i.e. the theoretical capacity, 2 Li equivalents, in 100 h) in the potential range 0.01–2.00 V.

3. Results and discussion

The pristine TiH_2 (Sample A) shows a very limited crystallinity: the corresponding XRD pattern is shown in the Fig. 1A. The diffraction pattern is featureless besides a possible small and broad peak at $2\theta \approx 35.0^\circ$, indicated by an arrow in the Fig. 1A, that may be indexed to the (111) reflection of the $\alpha\text{-TiH}_2$ phase (CaF_2 -type cubic lattice Fm-3m spacegroup and cell parameter $a = 4.54 \text{ \AA}$) [7]. Also ball milled samples show very low crystallinity: no diffraction peaks have been observed after ball milling without or with carbon (data are omitted as all diffractograms are featureless and therefore banal). Morphological details about the properties of the pristine and milled samples are provided by TEM observations. Transmission electron micrographs are shown in Fig. 1. Apparently the pristine Sample A material is constituted by irregular TiH_2 aggregates of nanometric particles: this morphology is not strongly modified by the ball milling procedure, even when Super P is added. The only alteration observed in the B1D1 sample concerns the agglomeration of the Super P round particles with the almost unaltered nanometric TiH_2 aggregates.

The first discharge/charge voltage profiles in galvanostatic experiments of the three samples are shown in Fig. 2. During the

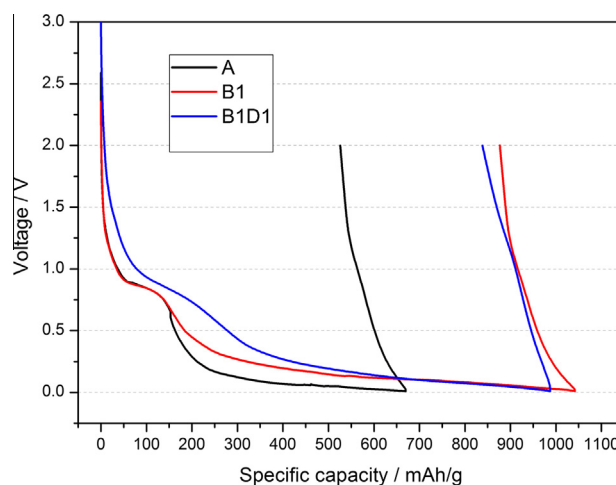


Fig. 2. Galvanostatic discharge/charge curves in lithium cells for all samples measured at C/100.

first discharge a capacity of ~ 670 , 1040 and 990 mA h/g is obtained for Sample A, B1 and B1D1, respectively. After ball milling, both samples B1 and B1D1 are able to deliver the whole theoretical capacity, corresponding to the complete conversion of $\text{TiH}_2 + 2\text{Li}^+ = \text{Ti} + 2\text{LiH}$. Surprisingly, even our pristine TiH_2 is able to discharge more than 60% of the theoretical value even without any mechanochemical pretreatment. This is in contrast with the

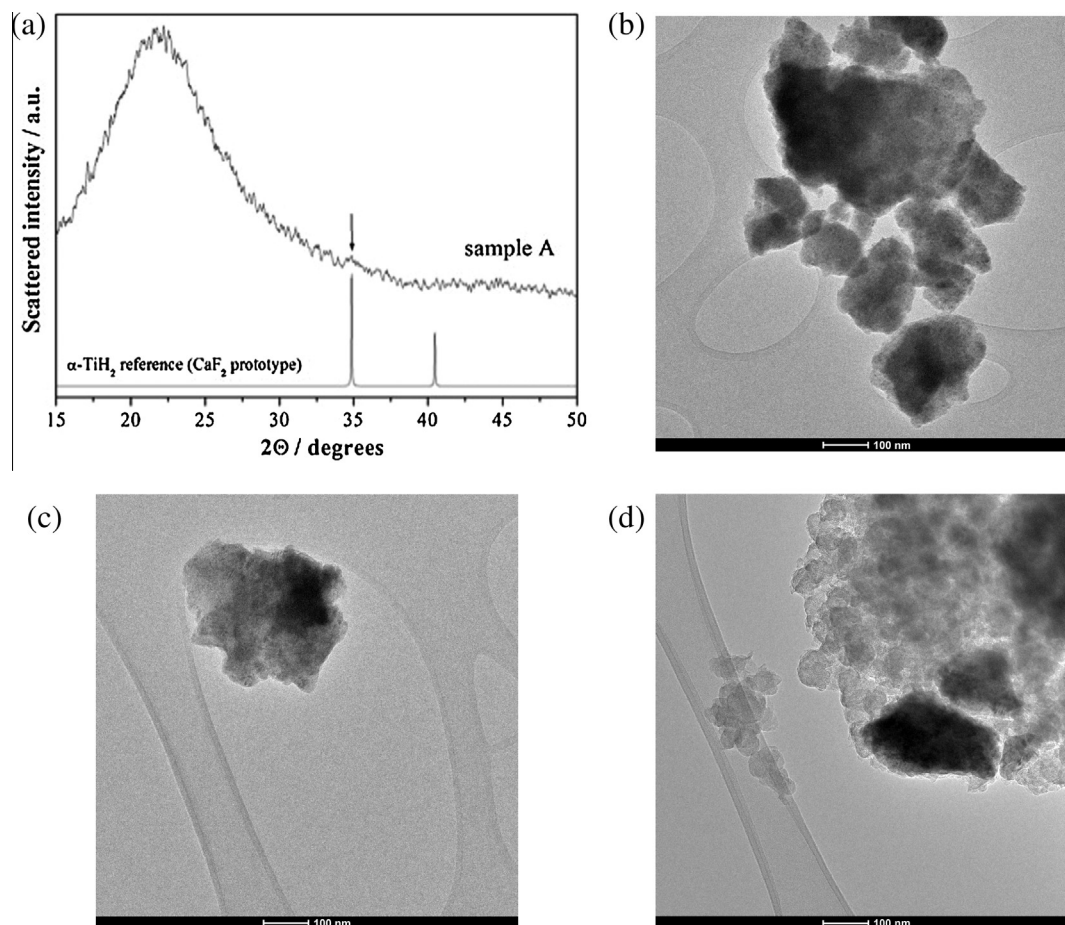


Fig. 1. XRD measurement of the pristine sample (upper left panel); TEM images of Sample A (upper right panel), B1 (lower left panel) and B1D1 (lower right panel).

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