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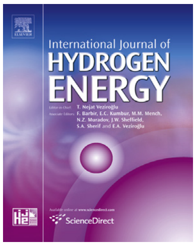

Synthesis of destabilized nanostructured lithium hydride via hydrogenation of lithium electrochemically inserted into graphite

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ABSTRACT

Lithium hydride-graphite composite is synthesized through hydrogenation of lithium intercalated graphite obtained by electrochemical insertion. XRD analysis indicates that the initial graphite is transformed into a mixture of LiC_6 and LiC_{12} by the intercalation of 0.84 lithium for six carbons. After 20 h of hydrogenation under 30 bars at 150 °C, these lithium-inserted compounds are completely transformed into a lithium hydride-graphite composite based on the reaction: $Li_{0.84}C_6 + 0.42H_2 \rightarrow 0.84LiH + 6C$. A weak shift and broadening of the (002) reflex of graphite is observed after the formation of LiH, which is attributed to a small increase of the graphite disorder. Thermal gravimetric analysis coupled with Mass Spectrometry (TG-MS) shows that the desorption of this synthesized nano-LiH starts from around 200 °C, which is much lower than the decomposition temperature (900 °C) of pure LiH. It reveals that this new electrochemical synthesis process of LiH-graphite composites enables an interesting destabilization of the Li–H ionic bond due to a good dispersion of highly divided LiH nanoparticles (below 100 nm) in a carbon matrix. The hydrogen storage capacity of this LiH-graphite composite can be increased by subsequent Li insertion/hydrogenation cycles.

Introduction

Metal hydrides, which are applied as negative electrode in Ni/MH (nickel-metal hydride) batteries [1] are also established as potential powerful hydrogen storage materials [2]. Amongst these hydrides, lithium hydride (LiH) is considered to be a promising candidate for hydrogen storage due to its high theoretical capacities, i.e. gravimetric capacity of 12.7 wt. % and volumetric capacity of 99 g H_2/L. However, the strong ionic bonding between Li and H makes LiH so stable

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that it requires 900 °C to release hydrogen at a pressure of 1 bar [3]. This high stability hinders its practical use for hydrogen storage [4] and therefore LiH needs to be destabilized to be considered for practical applications. In a first destabilization attempt, the addition of a third element is expected to be applicable for LiH. This technique is actually widely used for AB_y intermetallics with y equal to 0.5, 1, 2, 5; A and B are metals that tend to form stable and unstable hydrides, respectively. Graphite represents one promising additive because it can be inserted by lithium to form lithium intercalated graphite compounds such as LiC_6 and LiC_{12}. Luo et al. [5] investigated hydrogenation properties of LiC_6 and LiC_{12} prepared by mechanical mixing and pointed out that these two compounds showed enhanced hydrogenation reactivity relative to Li metal with formation of LiH achieved at 200 °C. Srinivas et al. [6] studied the hydrogenation properties of LiC_6 prepared by metal-vapor method and indicated that ternary compound production from LiC_6 and H_2 was not possible because hydrogenation led to a phase separation with graphite and LiH formation. However, dehydrogenation properties were not reported by these two articles. Miyaoka et al. [7] studied hydrogen sorption properties of (Li + 2C) ground mixture and revealed that the hydrogenated Li-graphite sample desorbed only H_2 from 150 °C with a complex mechanism since Li_2C_2, LiH and LiC_{12} were present after desorption. Thereafter, Isobe et al. [8] carried out microscopic characterization for these hydrogenated/dehydrogenated Li-graphite samples and indicated that LiH was generated at the edge site of graphite.

LiH combined with a metal can be furthermore considered as a significant candidate to be used as negative electrode for lithium-ion batteries. Our group has recently reported that several metal hydrides could be used for this purpose [9–13]. For instance, a reversible capacity of 1480 mAh g^{-1} at an average potential of 0.5 V versus Li^+/Li^0 is obtained for the reaction between MgH_2 and Li according to the conversion process $MgH_2 + 2Li^+ + 2e^- \rightleftharpoons Mg + 2LiH$. This reaction can be initiated from a metal hydride (MH_x) or, interestingly, from an intimate mixture of a metal (M) and lithium hydride (LiH) (M + 2LiH) [13]. Moreover, this reaction produces nanosized Mg and MgH_2, with a particle size ranging between 10 nm and 30 nm (Mg) and 10 nm–40 nm (MgH_2), which shows attractive enhanced hydrogen sorption/desorption properties [12]. As a result, one the one hand, hydrogen storage and lithium-ion batteries technologies can be bridged and, on the other hand, electrochemical technique is proved to be effective to produce hydrogen storage materials with improved properties. However, the practical application of this conversion process needs stabilization of the nanoscale metal and LiH particles in a conductive matrix like carbon.

Pursuing this approach with the perspective to produce Mg/LiH-graphite electrode composite, the electrochemical lithium insertion is chosen in this work as a technique for preparing lithium intercalated graphite compound. This material is transformed into nanoscale LiH and graphite mixture by a subsequent hydrogenation. Stability of the as-obtained nanoscale LiH-graphite composite is then investigated and discussed.

Experimental

Raw MCMB 2528 graphite (mesocarbon microbeads, 2528 correspond to an average microbead size of 25 μm and a heat treatment at 2800 °C) was used as working electrode. Electrochemical tests at room temperature were performed in modified large Swagelok-type cells which could support large mass of samples (up to 0.5 g). The electrochemical cells were assembled in an argon filled glove box and tested using a VMP3 (Bio-Logic-Science Instruments) controlled by means of the EC-Lab software operating in galvanostatic mode with a cut off potential of 0.005 V versus Li^+/Li^0. These cells comprised (1) a 19.625 cm^2 disk of positive electrode containing 0.5 g of MCMB 2528 as the working electrode (2) a 19.625 cm^2 Li metal disk as the negative electrode and (3) a Whatman GF/D borosilicate glass fiber sheet saturated with a 1 M $LiPF_6$ electrolyte solution in 1:1 dimethyl carbonate (DMC)/ethylene carbonate (EC) as the separator/electrolyte. The cells were discharged at a rate of one lithium in 20 h vs. nominal LiC_6 composition. Once discharged down to the required potential 0.005 V versus Li^+/Li^0, the cells were stopped and opened in an argon filled glove box. The electrode material was recovered, rinsed with dimethyl carbonate (DMC) and dried. Afterwards, the obtained powders were loaded into a stainless steel vessel, hermetically sealed using screws and copper ring. The active material was then hydrogenated at 150 °C for 20 h under 30 bars of hydrogen pressure inside the stainless steel vessel.

XRD patterns were carried out with a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). The electrode material was introduced in a beryllium window sealed cell for XRD analysis to avoid any oxidation by exposing to air during the measurement.

Thermal gravimetric analysis (TGA) were performed on a Simultaneous Thermal Analyzer STA 449 C Jupiter Unit (Netzsch), at a heating rate of 10 °C min^{-1} under a constant argon flow of 50 mL/min and from room temperature to 800 °C. Values of isothermal drift and sensitivity were 0.6 mg/h and 0.1 mg, respectively. This TGA apparatus was coupled with a Quadrupole QMS 403 Aeolos mass spectrometer (Detector SEV/Sekundär Elektronen Vervielfacher (Channeltron), stainless steel capillary, counting time 20 ms per m/z with a resting time of 1 s, scanning width 1/51 amu).

Microstructural analyses were performed by Transmission Electron Microscopy (TEM-Tecnai F20 with a Field Emission Gun 200 KV). A special Gatan air-tight sample holder was used for TEM sample transfer under protective atmosphere. The sample holder was cooled down to −160 °C to avoid sample decomposition by beam irradiation in the microscope. In order to determine LiH phase distribution within the carbon, (P) ACOM-TEM (Precession Automated Crystal Orientation Mapping) technique has been employed. This automated technique is based on template matching between the electron diffraction pattern acquired in TEM and the calculated ones with the ASTAR package [14,15]. More precisely, the ASTAR automatic crystallographic indexing and orientation/phase mapping tool was used in TEM mode with spot 8, guns lens 6, a 10 μm C2 aperture, a probe with 1.2 nm diameter and