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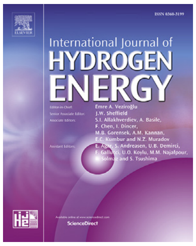

Dual-tuning the thermodynamics and kinetics: Magnesium-naphthalocyanine nanocomposite for low temperature hydrogen cycling

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ABSTRACT

2,11,20,29-Tetra-*tert*-butyl-2,3-naphthalocyanine (TTBNc) was used as an alternative host to support magnesium (Mg) nanoparticles. After deposition and decomposition of dibutylmagnesium on TTBNc, Mg nanoparticles of around 4 nm supported on TTBNc were observed by TEM. These TTBNc stabilized Mg nanoparticles were found to absorb hydrogen at 100 °C and release hydrogen from 75 °C. The Mg-TTBNc material showed good hydrogen cycling properties and structural stability. Kinetic measurements showed fast hydrogen absorption within 2 min at 150 °C. The hydrogen desorption kinetics were slower at the same temperature but faster at 250 °C with 80% of the hydrogen desorbed within 1 h. Enthalpy and entropy for hydrogen uptake and release in Mg-TTBNc determined from PCT measurements were found to be of 52.7 ± 4.9 kJ mol^{-1} H_2 and 107.8 ± 9.4 J K^{-1} mol^{-1} H_2, respectively. These values are much lower than those of bulk Mg.

Introduction

Possessing high theoretical storage capacity (7.6 mass%) and good reversibility, magnesium (Mg) is considered as a promising material for hydrogen storage [1]. However, the high temperature required for Mg to reversibly store hydrogen (>300 °C) remains the main obstacle for practical use. Dual-tuning of the thermodynamics and kinetics is thus a key issue for the improvement of the hydrogen storage properties of Mg. Doping/alloying with other elements (e.g. Al, In, Ti) is one approach [2–5], with potential for tuning both thermodynamics and kinetics, however the temperature for hydrogen release still remains high. In recent years, nanosizing has emerged as an alternative approach on the hypothesis that particle size effects at the nanoscale will lead to improved kinetics and thermodynamics toward low temperatures hydrogen uptake and release [6–12]. To verify such an assumption, intensive work has been carried out to prepare Mg nanoparticles smaller than 10 nm. In a typical synthesis, a mesoporous carbon scaffold is used to stabilize Mg nanoparticles against agglomeration. The later are generated from the impregnation of the scaffold with di-*n*-butylmagnesium ($MgBu_2$) and its hydrogenolysis [13,14], or by melt infiltration of Mg [15,16].

Initial investigations resulting from these synthetic approaches found that the final Mg particle size depends upon the pore size of the host scaffold [15]. Generally, a high

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temperature (>649 °C) is required to obtain Mg in a molten state. However, formation of large Mg particles (>100 nm) was observed when the temperature for melt infiltration was raised above 750 °C [16]. Impregnation and hydrogenation of $MgBu_2$ is an alternative approach that avoids the high temperature required by melt infiltration. Therefore, this approach is more commonly used for confining Mg nanoparticles within the porosity of carbon scaffolds. Through melt infiltration and $MgBu_2$ decomposition, Mg/MgH_2 nanoparticles with a size ranging from 1.3 to 20 nm have been nanoconfined [13,14,17–19] and in most cases, this led to a significant decrease in the hydrogen release temperature. For instance, MgH_2 (~4 nm) nanoconfined in CMK-3 showed a desorption temperature of 253 °C as compared to 395 °C for bulk MgH_2 [18]. P-doping of CMK-3 was found to further improve hydrogen desorption from nanoconfined MgH_2 with a lower temperature (<200 °C) for the hydrogen release [19]. Even lower desorption temperatures were observed for ultrasmall nanoconfined MgH_2 particles of 1.3 nm, which started to release hydrogen below 100 °C with a peak at 200 °C [9]. Altered thermodynamics have also been observed for nanoconfined MgH_2. For example, a desorption enthalpy of 52.4 ± 2.2 kJ mol^{-1} H_2 was reported for 4 nm MgH_2 confined in CMK-3 [18], and 3 nm MgH_2 particles confined in activated carbon fibres showed a reduced enthalpy of 63.8 kJ mol^{-1} H_2 instead of the 75 kJ mol^{-1} H_2 observed for bulk MgH_2 [14]. Such a reduction in enthalpy was attributed to a combination of particle size effects and strain due to the particle/support interaction. However, such a reduction in enthalpy is often compensated by a variation in entropy limiting the temperature for hydrogen desorption [14,20]. One drawback in the use of porous carbon materials for stabilising Mg nanoparticles is the low overall hydrogen storage capacity of the composite material (usually < 1 mass % H_2) owing to the dead mass and volume of the carbon scaffolds. An alternative would be to utilise 2D materials that can be fully covered on both sides with well stabilized and dispersed Mg nanoparticles. Most carbons involve oxygen surface groups which provide some sites for Mg nanoparticle nucleation and growth but also lead to a partial oxidation of the deposited Mg nanoparticles and thus a reduction of the overall hydrogen storage capacity.

Herein, we attempted to use 2,11,20,29-Tetra-*tert*-butyl-2,3-naphthalocyanine (TTBNc) as an alternative to carbon materials. TTBNc has nitrogen groups that could potentially act as anchor points for Mg nanoparticles and aromatic rings that could potentially facilitate some electronic delocalisation reducing the strength of the Mg-hydrogen bond (Scheme 1). Indeed, we found upon characterization of the hydrogen properties of this composite material that this strategy led to a significant reduction of the temperature for hydrogen release.

Materials and methods

All operations including material synthesis, handling and preparation for characterization were carried out under inert atmosphere in an argon-filled LC-Technology glove box (<1 ppm O_2 and H_2O).

Materials

1.0 M di-*n*-butylmagnesium ($MgBu_2$) solution in heptane and 2,11,20,29-Tetra-*tert*-butyl-2,3-naphthalocyanine (TTBNc) were purchased from Aldrich and used as received.

Synthesis of magnesium-porphyrin nanocomposites

In a typical synthesis, $MgBu_2$ solution was added on 60 mg TTBNc dropwise (Scheme 1). The mixture was stirred for 1 h before drying overnight under vacuum on Schlenk line with stirring. Then the dried mixture was decomposed in tube furnace for 1 h under vacuum at elevated temperatures. The final material is noted of Mg-TTBNc. Effects of the decomposition temperature were tested by carrying out the decomposition at 250, 300 and 350 °C with a fixed Mg loading (40%). Different Mg loadings 20, 40, 60 and 80% were also tested by varying the volume of $MgBu_2$ solution added. For reference, “pristine” Mg (noted as 100%) was obtained from the decomposition of $MgBu_2$ following the same synthetic procedure. It should be noted that the Mg loading corresponds to the theoretical Mg content in the material after the decomposition of $MgBu_2$.

Characterization

The surface area of the material was determined by BET measurement which was performed using a Micromeritics TriStar 3000 Analyser from Micrometrics Instrument Corporation. The material was degassed at 150 °C for 3 h prior to the measurement and the measurement was performed by adsorption of N_2 at 77 K.

The morphology, local structure and chemical composition were analysed by Transmission Electron Microscopy (TEM) using a Philips CM200 operated at 200 kV. The materials were first dispersed in tetrahydrofuran, sonicated for a few minutes and then dropped onto carbon coated copper grid for TEM analysis. Particle size distribution of the obtained materials was measured based on high resolution TEM images using Nano Measurer.

The crystalline nature of the materials was determined by X-Ray Diffraction (XRD) using a Philips X'pert Multipurpose XRD system operated at 40 mA and 45 kV with a monochromatic Cu Ka radiation ($\lambda = 1.541$ Å)—step size = 0.01, 0.02 or 0.05°, time per step = 10 or 20 s step^{-1}. The materials were protected against oxidation from air by a Kapton foil. Crystallize size was determined using the Scherrer equation.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) in conjunction with Mass Spectrometry (MS) were conducted at 10 °C min^{-1} under an Argon flow of 20 mL min^{-1} using a Mettler Toledo TGA/DSC 1 coupled with an Omnistar MS. Masses between m/e = 2 and 100 were followed and alumina crucibles were used.

Hydrogen cycling properties, including kinetics and Pressure Composition Temperature (PCT) curves were determined by using a high-pressure magnetic balance of 1 μg resolution equipped with capability for simultaneous density measurements (Rubotherm). Around 70 mg of material was used, with a hydrogen pressure of 6 MPa for absorption and 0.01 MPa for

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