

Low-temperature hydrogen desorption and the structural properties of spark discharge generated Mg nanoparticles

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Abstract

Mg nanoparticles were synthesized using spark discharge, resulting in large-scale structures of agglomerated nanoparticles with primary particle sizes of ~ 10 nm, surrounded by MgO shells 1–2 nm thick. Thermal hydrogen desorption starts at remarkably low temperatures of ~ 350 K, related to the small sizes of particles, and extends over a broad temperature range to beyond 700 K, caused by the presence of oxide shells acting as activation barriers. The hydrogen sorption kinetics is increased significantly by adding Pd nanoparticles in situ during synthesis, showing the versatility of spark discharge generation for the production of metal hydride nanocomposites.

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1. Introduction

In a future sustainable energy economy, hydrogen may serve as a clean energy carrier, helping to reduce (and eventually eliminate) carbon dioxide and other greenhouse emissions. A major challenge is to achieve safe and reliable hydrogen storage technologies that meet the sometimes conflicting requirements of operating conditions, performance and cost [1–3]. During the last decade, there has been growing interest in the development of lightweight metal hydrides capable of reversible hydrogen storage at low and medium temperatures [2–4]. Their high volumetric hydrogen capacity may help to overcome the technological limitations of high-pressure hydrogen storage tanks and offer a route to economically viable hydrogen storage systems [5].

Magnesium hydride is a promising hydrogen storage material, with a high gravimetric storage capacity of up

to 7.6 wt.%. Further, Mg is abundantly available and cheap. However, the uptake and discharge of hydrogen proceeds slowly and at low hydrogen equilibrium pressures for practical operating temperatures below ~ 100 °C.

These properties can be improved by turning to nano-scale MgH_2 particle sizes. In this way, hydrogen diffusion can be greatly accelerated because of the small diffusion distances. Interesting non-stoichiometric magnesium hydride phases with abundant hydrogen vacancies appear during hydrogen cycling of ball-milled powders for grain sizes below ~ 100 nm using suitable catalyst additives [6,7], leading to further improved hydrogen kinetics. Recent studies showed that grain sizes can be kept small, typically 30–100 nm, as a consequence of the grain refinement action of added finely dispersed catalysts [6,8,9]. Finally, the thermodynamic properties related to the Mg– MgH_2 phase transformation may change as a function of size. Ab initio studies by Wagemans et al. [10] showed that the enthalpy of formation of MgH_2 is largely reduced for particle sizes below ~ 1.9 nm. Reduced hydrogen desorption temperatures for NaAlH_4 , embedded as nanoparticles

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in carbon frameworks by melt infiltration synthesis, were observed by Baldé et al. [11]. The reduced desorption temperatures can be related to significant changes in hydrogen sorption kinetics [12] and phase diagrams [13] for metal hydride nanoparticles [14].

In our previous study on spark discharge generated (SDG) Pd nanoparticles [12], we demonstrated that the hydrogen uptake and release kinetics is largely enhanced compared to Pd foils. A transition from diffusion-limited kinetics for bulk Pd to surface-activated desorption kinetics for Pd nanoparticles was observed [12], leading to significantly reduced hydrogen desorption temperatures. Further, increased hydrogen desorption pressures were detected. Therefore, we investigated whether such beneficial changes also occur for SDG Mg nanoparticles. In the case of ball-milled Mg powders, it is well known that the inclusion of catalysts improves the hydrogen sorption kinetics [15,16]. By adding a second spark generator for catalyst particles, their concentration can be controlled simply by setting the relative spark frequencies of the two spark generators. Mixing of the catalyst and metal hydride particles then takes place in the gas phase, and this can greatly enhance the dispersion of the catalyst.

In brief, in SDG, a high-voltage power supply is used to charge a capacitor bank connected in parallel to a spark gap between two electrodes (Fig. 1). A flow of carrier gas, typically Ar, He or N₂, is applied between the electrodes. In a discharge cycle, the voltage over the spark gap is increased relatively slowly until the breakdown voltage of the gas between the electrodes is reached, and a conductive channel is formed. The energy stored in the capacitor bank is released into the spark gap very rapidly, resulting in very high temperatures [17]. As a consequence, vapour jets emerge from the electrodes. As the discharge dies out, the cloud of formed material cools at extremely high cooling rates, resulting in a high concentration of very small nucleated clusters which grow through coalescence into bigger primary particles (2–10 nm). The particles then aggregate and form larger scale agglomerates [18]. The particles are subsequently carried away by a flow of inert gas and collected from the gas on a filter.

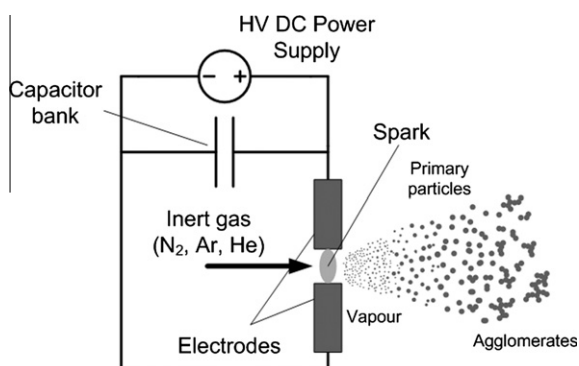


Fig. 1. Schematic diagram of the spark discharge process used for nanoparticle generation.

In this work, the hydrogen storage properties of Mg nanoparticles generated using spark discharge are analyzed. We will show that hydrogen desorption starts at significantly lower temperatures than commonly observed for ball-milled catalyzed MgH₂. The addition of a small fraction of Pd nanoparticles as a catalyst is seen to enhance significantly the hydrogen absorption and desorption kinetics. Furthermore, the evolution of the morphology and particle sizes upon hydrogen cycling is analyzed using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2. Experimental

2.1. Spark discharge generation

The synthesis of samples consisting of Mg nanoparticles and of mixtures of Mg and Pd nanoparticles was performed using a homebuilt spark discharge setup (Fig. 2) [12]. Two Mg rods (99.9+ % purity, Mateck GmbH) of ¼ in. diameter were used as electrodes of the first spark generator, which were sparked at a capacitor charging current of 12 mA, with a capacitance of 20 nF and a gap distance of 2 mm. For the synthesis of the Mg/Pd nanocomposites, a dual spark generator was used to add the catalyst nanoparticles to the Mg nanoparticles (Fig. 2). Two Pd catalyst electrodes with a diameter of 2 mm (99.95% pure, Goodfellow) were mounted in the second, bottom spark generator in a similar configuration. Both Mg and Mg/Pd nanopowders could be produced in this way by turning the Pd spark generator off or on. In the synthesis of Pd nanoparticles, a gap spacing of 2 mm was used, in this case with a capacitance of 10 nF and a discharge frequency of 3 Hz in order to achieve on the order of ~1 wt.% of Pd in the nanocomposite samples [18]. The nanoparticles were subsequently collected on Millipore Durapore 0.45 µm PVDF membrane filters held in a special filter holder perpendicular to the gas flow positioned

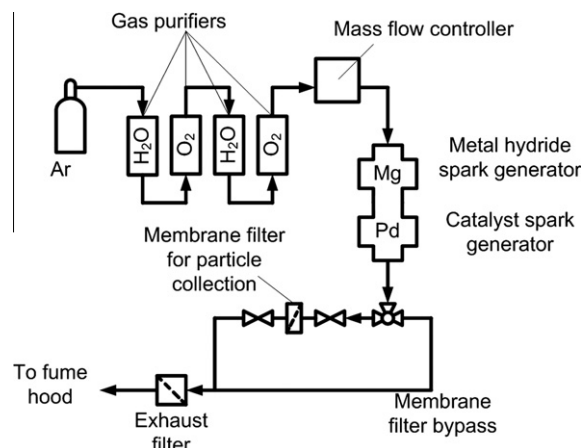


Fig. 2. Schematic diagram of the spark discharge set-up for the production of Mg and Mg/Pd nanoparticles.

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