High strength metallurgical graphene for hydrogen storage nanocomposites

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ABSTRACT

This work presents the results of an investigation on the atomic hydrogen chemisorption of metallurgical graphene enhanced by plasma discharge at low pressures in the range of 5–20 Pa. It was experimentally revealed that hydrogenated graphene is not stable when in contact with humid oxygen or humid air. Moreover, thermal desorption experiments showed that hydrogen can be released from hydrogenated graphene at relatively low temperatures. Additionally, a numerical simulations were performed of the pressure changes inside the nanogaps of hydrogen storage nanocomposites under various durations of the desorption cycle. Experimental fatigue resistance tests performed along with simultaneous electrical resistance measurements of the graphene sheets were also conducted. Metallurgical graphene shows tensile fatigue performances that might be sufficient to resist the pressure pulses and strain that arise in the gaps of graphene-based hydrogen storage systems.

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1. Introduction

Graphene-based nanomaterials appear promising for hydrogen-based fuel systems, as its theoretically estimated surface specific area (~2630 m^2/g) is much higher than that of other carbon structures providing a favorable platform for surface chemistry [1,2]. Other structural features of graphene (e.g., its tunable porosity, light weight and high thermal and chemical stability) could allow for the integration of a hydrogen-storage module into flexible and light graphene-based devices.

Three mechanisms of hydrogen sorption in graphene-based materials are considered: physisorption (interaction is caused by van der Waals force), chemisorption (involving a chemical reaction between the graphene and the hydrogen atom) and electrochemical sorption (an accumulation of ions or organic substances on the interface metal-solution as a result of electrostatic interactions and chemical adsorption). Recently, hydrogen storage in carbon nanomaterials is mostly based on physisorption on the surfaces and depends mainly on the electrostatic and dispersion interactions [3–8]. Physisorption usually happens with hydrogen in the molecular form. According to the work of Patchkovskii et al. [9],

the adsorption capacity of hydrogen strongly depends on the distances between the carbon planes within graphene. The theoretical physical adsorption of a monolayer of H_2 on a single side of the graphene surface can lead to approximately 3 wt% of H_2 (H/C = 0.18) [10]. However, from a thermodynamic viewpoint, it is impossible for H_2 molecules to penetrate between the graphene layers of graphite. The best results in hydrogen storage are achieved by maintaining the distance between the graphene planes in the range of 4–6 Å. A maximum of ~3.3 wt% H_2 is accomplished with one monolayer of adsorption between two graphene layers separated by 6 Å, for which up to 16 kJ/mol binding energy is obtained [11,12]. The binding energy decreases for larger interlayer spacing due to the second graphene layer. Therefore, it is important to build pillared 3D constructions between graphene sheets to provide the optimum interlayer spacing (e.g., Li dopants, in which interlayer spacing of approximately 6 Å with Li:C = 1:6 provides over 3 wt% H_2 adsorption). This interlayer spacing [9] or pore width [13] permits H_2 molecules to interact with both sides of the monolayer graphene. Therefore, the spatial distribution of molecular hydrogen adsorption on the graphene plane is delocalized. The H_2 interaction with graphene in bulk graphite is a localized phenomenon; therefore, adsorption is generally restricted to the external graphene sheet [14]. One of the main disadvantages of physisorption in the process of hydrogen storage is the very weak interaction energy ~0.01–0.1 eV, and physisorption can only be observed for low

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temperature and high pressure conditions, thereby significantly limiting the potential application range.

Due to the presence of free electrons in the carbon atom, reversible sorption of hydrogen could be more effective by chemisorption. A significant decrease of hydrogen volume and pressure occurs during its chemisorption as the result of the change in the chemical bond from H−H toward C−H. The chemisorption of molecular hydrogen on graphene presents a quantum barrier of approximately ~1.5 eV [15] because it requires the dissociation of H_2. From a hydrogen storage point of view, the maximum achievable gravimetric density in graphene through chemisorption is 8.3%, forming of a completely saturated graphene sheet, with 1:1 C vs. H stoichiometry. Hydrogenated graphene (graphane) contains covalently bonded hydrogen atoms to carbon atoms; therefore, the sp^3 C−H bonds on the basal plane are essentially different from the physical H_2 absorbed graphene structures. Furthermore, spectroscopic studies exhibit the appearance of sp^3 C−H bonds, and the hydrogen can be released upon heating or UV/laser irradiation, resulting in a sudden increase of gas volume during the hydrogen desorption step [16].

Various synthesis methods, such as plasma, CVD and liquid and gas phase reactions, have been developed to obtain hydrogenated graphene. Subrahmanyam et al. demonstrated that it could be used as a chemical H_2 storage material [17] reaching experimental hydrogen concentrations of up to 7.4 wt% [18−20]. Goler et al. [21] showed that by controlling the curvature of corrugated graphene sheets, an appropriate material for hydrogen storage applications could be created. Taking the above references into consideration, a state-of-the-art graphene nanocomposite structure GraphRoll has been proposed [22]. GraphRoll and other nanocomposite structures based on graphene must provide good physical and mechanical properties (close to the theoretical ones) to be considered efficient and reliable materials for the chemical sorption/desorption of hydrogen. It should show sufficient fatigue resistance, as it must be resistant to the temperature and pressure pulsation. Therefore, new technology for the growth of graphene on a liquid metallic matrix was developed leading to the creation of high strength metallurgical graphene (HSMG) [23,24].

This work presents the results of an investigation of the atomic hydrogen chemisorption on metallurgical graphene enhanced by plasma discharge as well as a numerical simulation of the pressure changes inside the nanogaps in hydrogen-storable nanocomposites during the desorption cycles. Additionally, experimental fatigue resistance tests combined with simultaneous resistance measurements of graphene sheets were conducted to demonstrate the superior mechanical properties of the metallurgical graphene compared to graphene grown by CVD.

2. Materials and methods

The HSMG sheets were synthesized in an industrially scaled thermochemical facility based on the process described by Kula and Kolodziejczyk [23,25]. The multilayer copper/nickel composite substrate (in this case 72% Cu, 28% Ni), was heated to the temperature of 1200−1250 °C in argon protective atmosphere at the constant pressure of 100 kPa. Then the chamber was evacuated to the pressure of 2 Pa and the mixture of acetylene, hydrogen and ethylene in the proportions of 2:1:2, at the partial pressure of 3 kPa, has been simultaneously introduced with argon into the process chamber for 1 min. Afterwards, the plate was cooled to the temperature of 1050 °C and then to the room temperature at the cooling speed of 0.5 °C/min and 5−10 °C/min, respectively, in argon atmosphere at the constant pressure of 100 kPa. Prior to the mechanical and electrical property investigations, all of the samples were subjected to structural analyses. The Raman spectra were

measured with a 100× objective at 532 nm with use of an inVia Renishaw spectrometer. The laser power on the sample was kept significantly below 1 mW to avoid possible laser-induced heating.

2.1. Sorption/desorption characteristics

The sorption and desorption of hydrogen on the surface of the polycrystalline HSMG graphene was investigated in a vacuum/low pressure chamber equipped with a vacuum pump and gas flow system. The level of hydrogen chemisorption was assessed by the measurement of the electrical resistance of the graphene sheet as a result of its free electrons' (charge carriers) involvement in the C−H bonds. A graphene sample was placed on an optical glass Schott B270 Superwite substrate with $25 \times 25 \times 1$ mm dimensions (Fig. 1). Gold electrodes were deposited such that the active surface area of the graphene was approximately ~1 cm^2.

A sample of metallurgical graphene was placed in a vacuum chamber from which air was evacuated to a pressure of $8 \cdot 10^{-3}$ Pa. Then, argon was introduced to purge the chamber of residual air. The atomic hydrogen chemisorption process was performed in a reactor filled with hydrogen at a pressure of 5−20 Pa. For the dissociation of hydrogen, a glow discharge generated by a 50 Hz alternating voltage between the electrodes at a height of 10 cm above the surface of the graphene was used. The desorption process took place in ambient air at a normal pressure or alternatively in the reactor chamber by introducing oxygen with a small amount of water vapor. The measured resistance value has been normalized. The entire procedure was then repeated five times to obtain the cyclic sorption/desorption characteristics. The hydrogenated graphene specimens were also heated in a low-pressure hydrogen environment to demonstrate the possibility of thermal hydrogen desorption from hydrogenated graphene. For this purpose, the hydrogenated graphene samples after the chemisorption process were heated to a temperature of approximately 150 °C. Both chemisorption and subsequent thermal desorption processes were carried out in the same hydrogen atmosphere at a pressure of 5 Pa. The resistance of the graphene was measured continuously during experiment.

2.2. Tensile tests
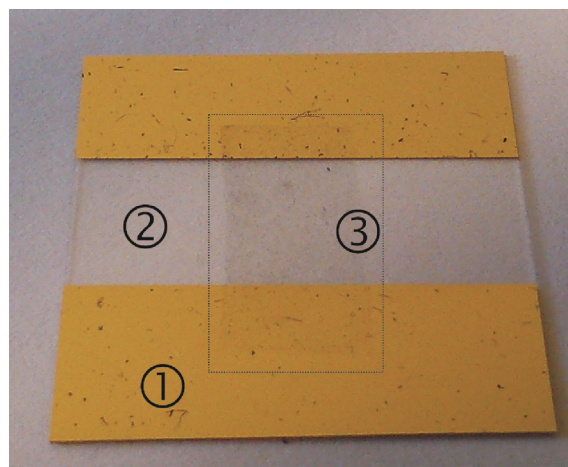
Cyclic tensile tests of the HSMG and CVD graphene

Fig. 1. HSMG graphene sample on the glass substrate that was used in the hydrogen sorption/desorption test: 1 − gold electrodes; 2 − substrate; 3 − graphene. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)