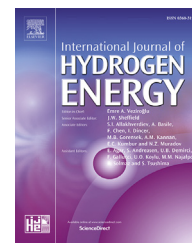




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# Enhanced hydrogen storage in graphitic carbon micro-nanofibers at moderate temperature and pressure: Synergistic interaction of asymmetrically-dispersed nickel-ceria nanoparticles

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## ABSTRACT

Nickel (Ni) and ceria (CeO<sub>2</sub>) nanoparticles (NPs) containing microporous and graphitic carbon nanofiber (CNF)-activated carbon microfiber (ACF)-based adsorbent was prepared as an efficient hydrogen (H<sub>2</sub>) storage material at 200 °C and 1 bar. The prepared Ni–CeO<sub>2</sub>-ACF/CNF was tested for the H<sub>2</sub> storage capacity under batch (static) as well as dynamic (flow) conditions, and the amounts of H<sub>2</sub> adsorbed were measured to be approximately the same. In its multiple roles, Ni NP served as the chemical vapor deposition catalyst to grow the CNFs on ACF, besides enhancing H<sub>2</sub> adsorption via the spillover mechanism, and decreasing the reduction temperature of CeO<sub>2</sub>. The experimental data corroborated the positive effects of the synergistic interaction between the Ni and CeO<sub>2</sub> NPs and the graphitic characteristics of the CNFs on H<sub>2</sub> adsorption. Although CeO<sub>2</sub> induced irreversibility in H<sub>2</sub> adsorption on Ni–CeO<sub>2</sub>-ACF/CNF, the adsorbent was completely regenerated at 300 °C and 1 bar, indicating the developed H<sub>2</sub> storage-regeneration process in this study to be effective, practical, and energy efficient.

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## Introduction

In view of globally rapid depletion of fossil fuels and simultaneous increase in greenhouse gas emissions, there are burgeoning efforts to find alternative energy sources [1,2]. Hydrogen (H<sub>2</sub>) is considered to be alternative to fossil fuels as an energy source because of its clean and renewable characteristics and large abundance. One of the main challenges

associated with the practical usage of H<sub>2</sub> as a fuel is the development of an efficient and sustainable light weight on-board H<sub>2</sub> storage system [2–4].

Carbon-based nanostructured materials such as carbon nanofiber (CNF) and carbon nanotube (CNT) have been the focus of several recent studies, as the H<sub>2</sub> storage materials because of high surface area, small mass density, good thermal and chemical stability, and low cost of the materials [4]. There are different mechanisms proposed for the adsorption

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of H<sub>2</sub> in CNFs and CNTs. Browning et al. measured the H<sub>2</sub> storage capacity of 0.055% (w/w) in CNF at 25 °C and 1 bar and attributed the adsorption to the active sites in the material [5]. Specifically, H<sub>2</sub> molecules were indicated to be catalytically dissociated by the edges of the graphitic planes in the CNFs at room temperature (~25 °C). The dissociated H-atoms slipped in the interlayer spacing of the nanofibers and were adsorbed at the surface. The exposed free edges of hexagons with several hetero-atoms present in CNFs have also been indicated to provide active adsorption and catalytic sites to other gases such as NO<sub>x</sub> and SO<sub>x</sub>, resulting in the dissociation of the species molecules [6,7]. Adsorption of H<sub>2</sub> in CNTs is also reported at room temperature and 1 bar. Rather et al. measured the H<sub>2</sub> storage capacity of 0.1% (w/w) at 25 °C and 1 bar [8]. The capacity increased to ~0.2% (w/w) at 19 bar. The authors proposed the adsorption of H<sub>2</sub>, however, without dissociation on the exterior and interior walls of the CNTs and in void regions between the CNTs. Wu et al. measured the H<sub>2</sub> storage capacity of ~1.60% (w/w) in CNTs at room temperature and 30 bar [9]. In this case also, physisorption on the exterior and interior surfaces of the CNTs was stated to be the mechanism for H<sub>2</sub>-adsorption. Interestingly, Barghi et al. reported chemisorption along with physisorption for H<sub>2</sub> in CNTs, leading to hysteresis in the adsorption-desorption isotherms [10]. The authors quantified the contributions from physisorption and chemisorption to be 0.13 and 0.058% (w/w), respectively, at 25 °C and 100 bar.

With a view to increasing H<sub>2</sub> storage capacity in CNTs/CNFs, adsorption has been performed at cryogenic temperature. In such case, internal surface area of the material is stated to be the controlling factor for the increased capacity. Ioannatos et al. measured the H<sub>2</sub> storage capacity of 3.27% (w/w) in CNTs at 1 bar and 77 K and proposed that H<sub>2</sub> was adsorbed on the interior/exterior surface and was also confined within the interstitial pores between the CNTs [11]. Lee et al. reported the H<sub>2</sub> storage capacity of 0.18% (w/w) in CNTs at 77 K and 1 bar, and proposed the same mechanism, i.e., the material retaining H<sub>2</sub> molecules at the inner surface of the individual tubes as well as within the pores of inter-tube spaces [12]. Similar level of H<sub>2</sub> adsorption capacity (~2.1% w/w) was measured in CNFs at 77 K and 1 bar [13]. The capacity increased to 3.4% at 20 bar, re-corroborating the internal or BET surface area (S<sub>BET</sub>) of the material to be responsible for the enhanced capacity via physisorption of H<sub>2</sub> molecules. From the overview of the above-cited studies, it is clear that either high pressures or cryogenic temperature is required to achieve a high H<sub>2</sub> storage capacity in CNTs/CNFs, thus rendering the process to be energy extensive.

CNTs/CNFs are often doped with noble metals to enhance H<sub>2</sub> storage capacity (~0.35–3.72% w/w) at room temperature (298 K) [14–19]. To cite a few salient studies, Park et al. studied the H<sub>2</sub> storage behavior of MWCNTs loaded with crystalline Pt particles, and reported the H<sub>2</sub> storage capacity of 3.72% (w/w) at 100 bar, which was ~2.5 folds higher than that of the pristine MWCNTs [14]. Yang et al. measured a H<sub>2</sub> storage capacity of 1.25% (w/w) at 100 bar for the Pt-doped MWCNTs dispersed in MOF-5, which was approximately two- and four-folds higher than that of Pt-MWCNTs and MOF-5, respectively [15]. Kim et al. fabricated nanoporous carbon fibers from polyacrylonitrile polymeric fibers coated with Pd

nanoparticles (NPs) and used the prepared material for H<sub>2</sub> storage [16]. The H<sub>2</sub> storage capacity was measured to be 0.35% (w/w) at 1 bar. Wenelska et al. studied the effect of different sizes of Pd NP dispersed in hollow carbon spheres and reported the maximum H<sub>2</sub> storage of ~0.36% (w/w) at 24 bar for the 11 nm-sized Pd NPs-dispersed spheres [17]. Lupu et al. prepared CNFs of herringbone conformation using chemical vapor deposition (CVD) on Pd/La<sub>2</sub>O<sub>3</sub> catalyst and measured H<sub>2</sub> storage capacity of 1.5% (w/w) at 100 bar [18]. Tsai et al. dispersed Pt NPs in CNTs using a hybrid method combining electroless deposition and the supercritical CO<sub>2</sub> fluid and reported a H<sub>2</sub> storage capacity of 2.7% (w/w) at 70 bar [19].

Doping of CNTs/CNFs with inexpensive Ni or Cu transition metal has also been shown to increase H<sub>2</sub> storage capacity (~0.7–2% w/w) at room temperature, although the storage pressures are high (50–100 bar) [13,20–24]. In such case, the metal (as well as carbon surface of the CNFs/CNTs) catalytically dissociates H<sub>2</sub> into atoms [3]. The H-atoms migrate and diffuse within the porous carbon substrate; such mechanism for H<sub>2</sub>-adsorption is termed as *spillover effect* [20,21]. In the recent most study [13], adsorption of H<sub>2</sub> in the Ni-doped CNFs at room temperature was experimentally demonstrated to be affected by metal, internal surface area of the carbon substrate as well as graphitic content of the material. In the context of further enhancing the H<sub>2</sub> storage capacity of CNFs, the present study focuses on the use of ceria (CeO<sub>2</sub>) along with the Ni metal NPs dispersed in the carbon substrate. The relative ease with which CeO<sub>2</sub> changes its state between +4 and +3 is responsible for its good catalytic activity [25]. Therefore, the synergistic interaction of the Ni and CeO<sub>2</sub> NPs is used in this study to achieve an increased H<sub>2</sub> storage capacity in CNFs under moderate temperature (<200 °C) and pressure (1 bar) conditions.

The use of CeO<sub>2</sub> along with the oxides of transition metals (Cu/Ni) in the H<sub>2</sub> storage material is not new, although very few studies have been performed in this context [26–29]. Specifically, Wrobel et al. measured H<sub>2</sub> storage capacity of 0.68% (w/w) in the Ni–Ce mixed oxides at 300 °C and 1 bar, prepared by co-precipitation method [26]. The molar ratio of Ce:Ni was determined to be ~0.2 in the prepared material. The authors attributed the increased H<sub>2</sub> storage capacity to the presence of the metal in the CeO<sub>2</sub> matrix, resulting in decrease in the reduction temperature of CeO<sub>2</sub> and greater expansion of its lattice as compared to that of pure CeO<sub>2</sub>. Jalowiecki-Duhamel et al. studied the effects of temperature and Ni:Ce molar ratio in the mixture of Ni- and Ce oxides on the H<sub>2</sub> storage capacity. A molar ratio of 0.7–1 in the mixed oxides yielded the capacity of 1.47% (w/w) at 250 °C and 1 bar [27]. The study showed that the inclusion of the metal in CeO<sub>2</sub> created relatively more anionic vacancies at low temperature, and greater expansion and insertion of H<sub>2</sub> in the fluorite lattice of CeO<sub>2</sub>. Both studies showed the Ni oxide-based catalyst to be performing better than the Cu oxide-based catalyst, when mixed with CeO<sub>2</sub>. Berlouis et al. synthesized the similar (Ni–Ce) oxide materials for H<sub>2</sub>-storage. In the aforementioned study, the authors showed the effects of calcination on the presence of crystalline and amorphous phases in the material [28]. The authors measured the H<sub>2</sub> storage capacity of 0.24% (w/w) in the uncalcined sample at 250 °C and 1 bar, which was ~10 times higher than that of the calcined sample. The

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