J|A|C|S
COMMUNICATIONS

An Enhanced Hydrogen Adsorption Enthalpy for Fluoride Intercalated Graphite Compounds

Hansong Cheng,*[,†] Xianwei Sha,[†] Liang Chen,[‡] Alan C. Cooper,[†] Maw-Lin Foo,[†] Garret C. Lau,[†] Wade H. Bailey III,[†] and Guido P. Pez[†]

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania 18195, and Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, P. R. China

Received September 23, 2009; E-mail: Chengh@airproducts.com

It has been widely recognized that improved hydrogen storage devices require new lightweight materials capable of interacting with molecular hydrogen via either physisorption or chemisorption.[1,2] This interaction must occur with an appropriate strength to enable the capture of hydrogen to be reversible under practical operating conditions of temperature and/or pressure. Porous hydrogen storage materials that store H_2 via physical adsorption have a perceived advantage for system heat removal during filling relative to most metal hydrides and chemical hydrides due to the relatively low enthalpy associated with physisorption. Most hydrogen storage materials in this class rely on physical adsorption due to van der Waals forces and/or electron density donation from the σ orbital of H_2 to an electrophile ("Kubas-type binding").[3] Here, we report a study of H_2 adsorption in graphite intercalation compounds (GICs) containing fluoride anions. In contrast to Kubas-type binding and alkali metal GICs,[4] the dominant mechanism of hydrogen binding in these materials is donation of electron density from a nucleophile to the σ* orbital of H_2. We show that these compounds exhibit a higher heat of adsorption at near-ambient temperatures than other porous H_2 storage materials, such as activated carbons and metal organic framework (MOF) compounds, and thus could potentially serve as practical H_2 storage media.

In gas-phase calculations, "naked" fluoride anions[5] and charge-separated ammonium fluoride salts[6] have been shown to interact strongly with molecular hydrogen. Sweany et al. have reported an experimental characterization of adducts of H_2 with CsF ion pairs.[7] The normally infrared-silent H_2 was perturbed by the salt, yielding spectra interpreted as arising from H_2 and CsF adducts, with as many as 3 H_2 molecules per CsF, where H_2 interacts primarily with the F^- anion. Based on frequency shifts showing a lengthening of the H−H bond, the interaction was attributed to the donation of electron density from the F^- anion to the H_2 antibonding σ* orbital.

Fluorous MOF containing covalent C−F bonds exhibited a large H_2 uptake at 77 K, but unusually high H_2 adsorption enthalpies were not reported.[8] Thus, the conceptual challenge is to devise solid-state materials which incorporate both the strong hydrogen interactions of "naked" fluoride and sufficient porosity. Chemical intercalation of graphite has been demonstrated to increase the H_2 adsorption capacity by creating porosity through intercalation and separation of the graphene layers as well as increasing the hydrogen affinity of the graphite through increased electron density. For example, the second-stage graphite intercalation complex KC_{24} has been shown to adsorb $2H_2$/K at 77 K corresponding to 1.2 wt % H_2.[9] Electron transfer from K to the graphene layers in this "donor type" GIC increases the heat of adsorption from −4 kJ/mol in native graphite to *ca.* −10 kJ/mol in KC_{24}. To date, there have been no examples of "acceptor type" GICs with a demonstrated appreciable hydrogen adsorption. Graphite fluorides represent a well-studied subset of acceptor GICs. A range of fluorination levels are accessible, and the nature of the C−F bonding evolves from ionic to semi-ionic to covalent as the decreasing C:F ratio approaches 1:1.[10]

We conducted *ab initio* molecular dynamics (AIMD) simulations at room temperature on H_2 in a GIC containing fluoride anions and subsequently synthesized fluoride GICs for isotherm measurements. The electronic energies were calculated with periodic density functional theory (DFT) under the local density approximation (LDA) employing the Perdew−Zunger exchange-correlation functional[11] coupled with a plane-wave basis set, while the AIMD simulation was performed in the constant NVE canonic ensemble using the Nosé thermostat.[12] Details of the computational method, material synthesis, and characterization can be found in the Supporting Information. The selected unit cell in our simulations contains 32 C and 8 F atoms. For maximum capacity, stage-1 GICs were studied with 1, 2, 12, and 24 H_2 molecules per unit cell, corresponding to 0.37−8.22 wt % H_2.

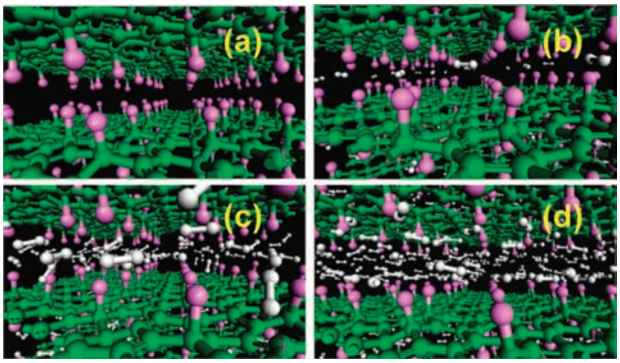

Figure 1. Fully optimized structures of the partially fluorinated GIC (a) and the GIC with 2 H_2 (b), 12 H_2 (c), and 24 H_2 (d).

Table 1. H_2 Gravimetric Density, the Calculated Lattice Spacing, the Average Bader Charge on F, and the Average H_2 Adsorption Energy at 300 K

complex	H_2 wt%	*d* (Å)	Q_F	Δ*E* (kJ/mol·H_2)
$C_{32}F_8$	–	5.698	−0.659	–
$C_{32}F_8 \cdot H_2$	0.37	5.613	−0.656	−23.3
$C_{32}F_8 \cdot 2H_2$	0.74	5.602	−0.655	−19.6
$C_{32}F_8 \cdot 12H_2$	4.29	6.556	−0.657	−10.5
$C_{32}F_8 \cdot 24H_2$	8.22	7.723	−0.656	−3.6

Upon F^- intercalation, significant lattice expansion (~2.3 Å) occurs, based upon the DFT structural optimization, and the intercalated F atoms form long C−F bonds with the graphene sheets. Compared to the typical C−F bond lengths in organofluorine compounds and perfluorinated graphite (~1.35 Å), the C−F bonds in the partially fluorinated graphite GIC are considerably longer, ranging from 1.417 to 1.533 Å. The significantly elongated, semi-ionic bonds arise from bond angle distortions resulting from the partial fluorination as only

---

[†] Air Products and Chemicals, Inc.
[‡] Chinese Academy of Sciences.

10.1021/ja907232y

some of the C atoms change their electronic configuration from sp^2 to sp^3. As shown in Table 1, Bader population analysis indicates that the average charge (Q_F) on the F atoms ranges from −0.655 to −0.659. At low H_2 loadings, the spacing between adjacent graphene layers shrinks slightly since the H_2 molecules interact more strongly with the semi-ionic F atoms (Table 1). At higher H_2 loadings, however, the interlayer distance increases substantially to accommodate the large number of H_2 molecules. Figure 1 displays the fully equilibrated structures of partially fluorinated GIC and GIC with 2, 12, and 24 H_2 molecules in the unit cell. A detailed analysis of the AIMD trajectories indicates that H_2 molecules in the lattice interact with the fluoride ions but are highly mobile in the interlayer spaces at 300 K. The H_2 molecules are confined to the interlayer spaces between F atoms and are rarely in close contact with graphene sheets. No dissociative chemisorption of H_2 was observed in the entire course of AIMD simulations. Our results suggest that the calculated average H_2 adsorption energy decreases as H_2 loading increases. At high H_2 loadings, the H_2-H_2 repulsion is largely responsible for the decrease of H_2 adsorption energy. At lower H_2 loadings, however, the simulation suggests that the average adsorption energy is substantially higher than those observed in most porous carbons.

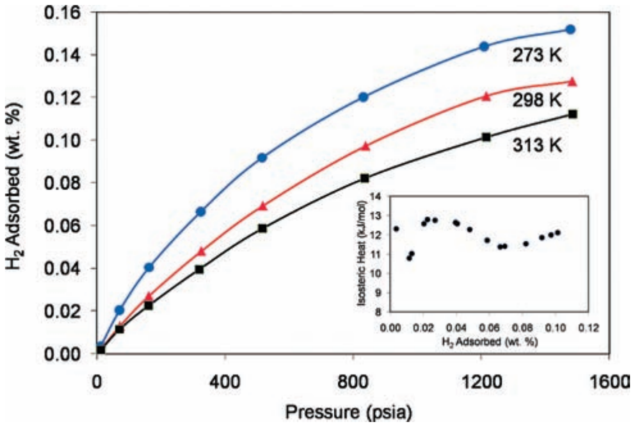

Figure 2. Hydrogen isotherms measured on $C_{22}F_{0.2}(BF_4)_{0.8}$ at 273, 298, and 313 K and the derived isosteric heat of adsorption.

To ascertain if partially fluorinated graphites are capable of adsorbing H_2, we synthesized a number of first- and second-stage fluoride GIC samples and subsequently measured H_2 isotherms and derived the isosteric heats of adsorption. Graphite fluoroborates, C_xBF_4, were synthesized in a manner similar to that of previous reports[13] by exposing crystalline graphite powder (Timrex SFG6, dried at 900 °C under argon) to a mixture of F_2 and BF_3 at room temperature. C_xBF_4 was then heated to 150 °C under vacuum, partially removing BF_3 from the lattice to form $C_xF(BF_4)_y$.[14] The partial decomposition of the C_xBF_4 was designed to yield a mixed GIC which contains both naked fluoride anions and residual BF_4 which could function as a "spacer" to sustain adequate interlayer spacing for the adsorption of H_2. Hydrogen isotherms on a number of $C_xF_y(BF_4)_{1-y}$ ($x = 8-26$, $y = 0.1-0.7$) samples were performed at pressures up to 1500 psia using differential pressure volumetric adsorption.[15] The isosteric heat of adsorption (heat of adsorption at equal H_2 coverage) revealed that partially fluorinated graphite can adsorb hydrogen at near-ambient temperatures with an enthalpy as large as *ca.* −12 kJ/mol of H_2 (Figure 2).

While this heat of adsorption is lower than what is predicted by the MD simulations performed at low H_2 loadings, the average enthalpy is higher than those reported for nonintercalated carbon materials such as graphite[16] (ca. −4 kJ/mol H_2 at 20 K and H_2 coverage of <0.9 mmol/g) or activated carbon[17] [−(6.5−5.0) kJ/mol H_2 at 77−273 K and H_2 coverage of 0−12 mmol/g]. The measured H_2 storage capacity of the GIC at near-ambient temperatures and the heat of adsorption are comparable to an MOF incorporating coordinatively unsaturated transition metals[18] despite the extremely large difference in surface area (see Supporting Information).

Besides the well-known LDA overbinding,[19] the gap between the calculated energies at low loading and the experimental heat of adsorption is likely due to the presence of residual BF_4 in the as-prepared GIC, which dilutes the gravimetric hydrogen density and adsorption enthalpy. After measuring isotherms on a large number of $C_xF_y(BF_4)_{1-y}$ samples, we found the isosteric heat of adsorption to be very sensitive to both the C:F ratio and the amount of residual BF_4. These variables likely affect the semi-ionic/covalent nature of the C−F bonds and accessibility of H_2 to the intercalated fluoride ions. It is apparent from the surface areas and H_2 uptake that only a fraction of the fluoride ions in the samples are accessible to H_2.

In summary, we propose a novel class of "acceptor type" GICs, which based on theoretical predictions and experimental evidence, can exhibit significantly higher isosteric heats of adsorption for H_2 than previously demonstrated for commonly available, porous carbon-based materials. The unusually strong interaction with H_2 arises from the semi-ionic nature of the C−F bonds. Although high H_2 storage capacity (>4 wt %) at near-ambient temperatures may not be feasible due to diminished heats of adsorption at very high H_2 densities, enhanced storage properties can be envisaged by doping the graphitic host with appropriate species (e.g., nitrogen) to promote higher levels of charge transfer from graphene to F^- anions. Synthetic strategies for increasing accessibility of hydrogen to the intercalated anions are also under development.

Acknowledgment. The authors gratefully acknowledge funding for this work provided by the U.S. DOE's Office of Energy Efficiency and Renewable Energy via the Hydrogen Sorption Center of Excellence (Contract DE-FC-05GO15074).

Note Added after ASAP Publication. Reference numbering was corrected Dec 9, 2009.

Supporting Information Available: Computational and experimental details and the MD trajectory for 12 H_2 molecules in the partially fluorinated GIC lattice in AVI format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schlapbach, L.; Züttel, A. *Nature* **2005**, *434*, 353.
(2) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283.
(3) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152.
(4) (a) Cheng, H.; Pez, G. P.; Kern, G.; Kresse, G.; Hafner, J. *J. Phys. Chem.* **2001**, *105*, 736. (b) Watanabe, K.; Soma, M.; Onishi, T.; Tamaru, K. *Nature* **1971**, *233*, 160.
(5) Nyulasi, B.; Kovacs, A. *Chem. Phys. Lett.* **2006**, *426*, 26.
(6) Trewin, A.; Darling, G. R.; Cooper, A. I. *New. J. Chem.* **2008**, *32*, 17.
(7) Sweany, R. L.; Ogden, J. S. *Inorg. Chem.* **1997**, *36*, 2523.
(8) Yang, C.; Wang, X.; Omary, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 15454.
(9) Watanabe, K.; Soma, M.; Onishi, T.; Tamaru, K. *Nature* **1971**, *233*, 160.
(10) (a) Watanabe, N.; Nakajima, T.; Touhara, H. *Graphite Fluorides*; Elsevier: Amsterdam, 1988. (b) *Fluorine-Carbon and Fluoride-Carbon Materials*; Nakajima, T., Ed.; Marcel Dekker: New York, 1995.
(11) Perdew, J.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048.
(12) Nosé, S. *J. Chem. Phys.* **1984**, *81*, 511.
(13) (a) Rosenthal, G. L.; Mallouk, T. E.; Bartlett, N. *Synth. Met.* **1984**, *9*, 433. (b) Brusilovsky, D.; Selig, H.; Vaknin, D.; Ohana, I.; Davidov, D. *Synth. Met.* **1988**, *23*, 377.
(14) Nikonorov, Y. I. *Kinetika i Kataliz* **1979**, *20*, 1598.
(15) Zielinski, J. M.; Coe, C. G.; Nickel, R. J.; Romeo, A. M.; Cooper, A. C.; Pez, G. P. *Adsorption* **2007**, *13*, 1.
(16) Pace, E. L.; Siebert, A. R. *J. Phys. Chem.* **1959**, *63*, 1398.
(17) Benard, P.; Chahine, R. *Langmuir* **2001**, *17*, 1950.
(18) (a) Dinca, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (b) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858.
(19) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

JA907232Y