

Graphite hydrogen storage properties in controlled reactive ball milling

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Abstract –Graphite was ball milled under argon and 500kPa hydrogen using two distinct mechanical milling modes: the shear and the impact. In the shear, absorbed was only to 0.5 wt% H, of which 50% can be released via heating to 500° C. In the impact, more than triple of this amount (1.9 wt %) was absorbed and only 16% desorbed under the same heating. The poor sorption in the sheared graphites is attributed to formation of short graphitic fragments divided by proliferation of stacking faults where H atoms are only weakly physisorbed. The higher adsorption and poor desorption in impacted graphite is traced to strong bonding in not-graphitic carbon clusters terminated with H, as observed in laser desorption mass spectroscopy experiment.

Phase transformations in graphite under mechanical treatment has been studied for almost 60 years and benefits of ball milling in the development of graphites for rechargeable batteries have been reported frequently over the last two decades [1]. Now, the same high-energy ball milling is used to increase specific surface area (SSA) for physisorption of gas H₂ for hydrogen storage for fuel cells. However, milling results also in proliferation of structural disorder in graphites and *mechanical activation* for H₂ sorption that may go beyond physisorption. Such a possibility was not thoroughly investigated. Recently, we reported chemisorbed hydrogen in ball-milled graphites. In ongoing project in our Wollongong and Ottawa groups, samples of graphite were ball milled under argon and hydrogen using a special ball mill that allows control over the mechanical (IMPACT or SHEAR) modes of milling. Changes to the microstructure were investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS) and Raman spectroscopy. The gases desorbed from the milled and the annealed samples were analyzed by CHN combustion analysis and laser-desorption flight-of-time mass (LDMS) spectroscopy [2]. The significant increase in the lattice c-parameter from 0.670 to 0.704 nm and shear bands in TEM photos give evidence to formation of turbostratic graphite during graphite shear, and destruction of hexagonal basal planes under ball impact (Figs. 1 and 2). Hydrogen absorption in shear and impact milled powders, as determined by CHN analysis was 0.53wt% and 1.85 wt%, of which 50% and 16% was desorbed up to 500°C, respectively. Although substantial H₂ absorption occurs on ball milling at ambient temperatures and pressures, H atoms seems to be strongly bonded in *nano-CH_x* carbon nanoclusters. Indeed, C₅, C₇ and C₈ clusters terminated with 1 to 4 H atoms were observed in the LDMS spectra [2]. These findings are compared to recent results published by other groups, viz. [3], which points to chemisorption in carbons activated in hydrogen ball mills. Available experimental data will be discussed as interplay between physisorption and chemisorption, and in terms of the stacking fault model we proposed previously in respect to H insertion into another layered compound (brucite-type Ni hydroxide) for electrochemical hydrogen storage [1].

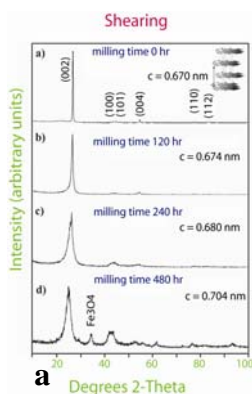


Figure 1: Starting graphite and graphite milled under hydrogen gas up to 480 h using mechanical SHEAR mode, **a)** XRD pattern **b)** TEM high resolution image. Red chevrons underline the shift of planes due to shearing forces during milling.

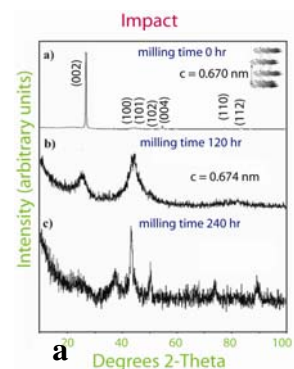
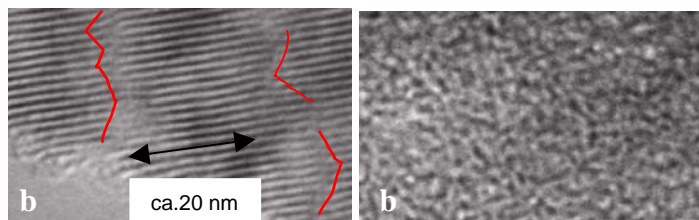


Figure 2: Starting graphite and graphite milled under hydrogen gas up to 240 h using mechanical IMPACT mode, **a)** XRD pattern **b)** TEM high resolution image.

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[3] C. Smith, H. Miyoka, T. Ichikawa, M. Jones, J. Harmer, W. Ishida, P. P. Edwards, Y. Kojima, H. Fuji, J. Phys. Chem. C 113(2009) 5409-5416