Diamond by-product of hydrogen production and storage method

June 23 2006

There may not be a pot of gold at the end of the rainbow, but there appears to be nanocrystalline diamonds at the end of a process to produce and store hydrogen using anthracite coal.

"The idea we explored was based on ball milling graphite processes found in the hydrogen storage literature," said Angela D. Lueking, assistant professor of energy and geoenvironmental engineering. "We substituted anthracite coal for graphite because it is abundant and inexpensive. Now, with 20/20 hindsight, we are struck by the fact that coal gasification is currently the most economical way to produce hydrogen."

Interest in hydrogen as a vehicular fuel has many researchers investigating ways to create hydrogen inexpensively; other researchers are looking at ways to transport and store hydrogen in a safe manner. Lueking's group was exploring a way to store hydrogen in carbon-based materials, and inadvertently stumbled upon a method that combines production and storage and produces nanocrystalline diamonds as a by-product.

Lueking and colleagues, who included Humberto R. Gutierrez, post doctoral fellow in physics; Dania A Fonseca, post doctoral fellow in the Penn State Energy Institute; Deepa L. Narayanan, Dirk Van Essendelft and Puja Jain, graduate students in energy and geoenvironmental engineering and Caroline E. B. Clifford, research associate, Energy Institute, ball milled powdered anthracite coal with cyclohexene. Ball

milling involves mixing a slurry of anthracite powder and cyclohexene with small steel balls and mixing so that the steel balls pound the coal particles and the cyclohexene causing physical and chemical changes. The researchers reported their results in a recent online issue of the Journal of the *American Chemical Society*.

"Ball milling imparts a lot of energy to the slurry," said Lueking. "There is high pressure and temperature in every impact of the balls on the slurry, but we do not really understand the structural changes in the carbon that occur in the process."

Lueking is puzzled because, unlike the graphite experiments, her anthracite experiment has hydrogen gas evolving from the mixture at room temperature. The hydrogen is either trapped in the material in a tight pore structure or a new carbon structure is being formed. The hydrogen outgassing continued for about a year and increased with addition of moderate heat.

"At first we thought the mass spectrograph was broken because hydrogen was just coming off," said Lueking. "We tried another mass spec and the same thing happened."

Wanting to know the structure of the ball milled product, and looking for carbon nanotubes, the researchers used transmission electron microscopy to investigate the small particles.

"When Gutierrez asked, 'do you know you have diamonds here?' our answer was no – we were not expecting to make diamonds," Lueking said.

What the researchers had were Bucky diamonds, a nanocrystalline diamond surrounded by onion–like layers of graphite. Diamonds are a natural form of pure carbon, but with a differing molecular structure

than graphite or the graphite-like coal.

"Bucky diamonds are relatively unexplored in terms of applications," said Lueking. "Nanocrystalline diamonds, however, have major industrial uses as abrasives and in electronics. These nanodiamonds are usually created by exploding TNT in a carbon source."

The ball milling process seems a simpler and gentler way of creating nanodiamonds and especially Bucky diamonds and Lueking's team hopes that once they understand how they are forming, they can increase the yield of diamonds in the process.

"At this point, we have not isolated the step that is forming the diamond," says the Penn State researcher. "The crystallization may be hydrogen-induced, it may be a result of the high temperatures and pressures within the mill, it may be a result of the processing we have done to purify the samples for transmission electron microscopy, or, it may be a combination of all of the above."

Lueking and her colleagues currently have a variety of experiments underway including looking at anthracite coal from different mines, looking at different hydrogenating compounds and trying to understand the mechanics of ball milling, the evolution of the hydrogen gas and the formation of the nanocrystalline diamonds and Bucky diamonds.

Source: Penn State