Green Car Congress
Energy, technologies, issues and policies for sustainable mobility

Print this post

UC Santa Barbara team develops catalytic molten metals for direct conversion of methane to hydrogen without forming CO2

17 November 2017

Researchers at the University of California Santa Barbara have developed catalytic molten metals to pyrolize methane to release hydrogen and to form solid carbon. The insoluble carbon floats to the surface of the melt, where it can be removed and stored or incorporated into composite materials. This method also avoids carbon formation on steam-reforming catalysts, which usually deactivates the catalysts.

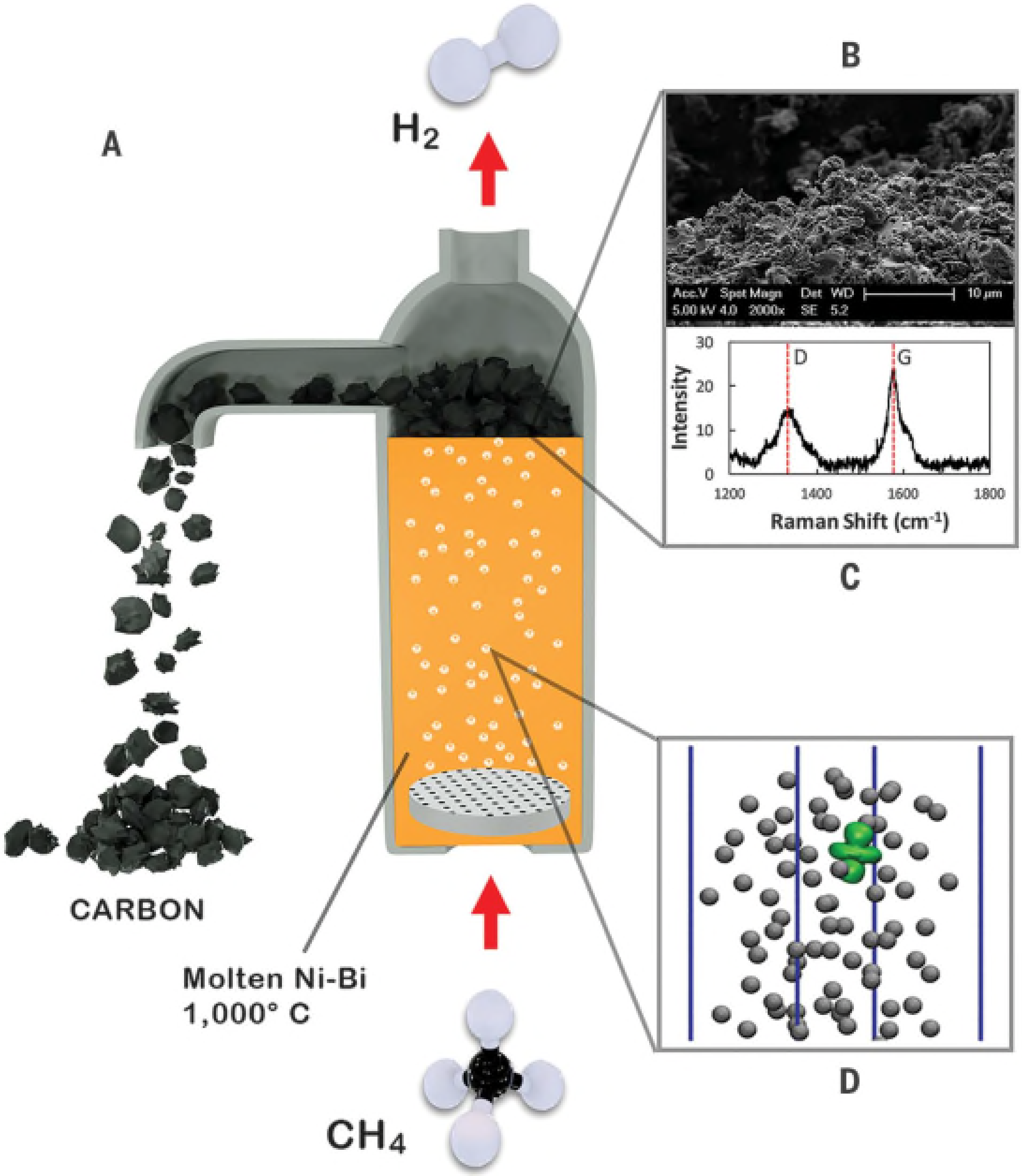
In a paper in the journal *Science*, the team reported that a 27% Ni–73% Bi alloy ($Ni_{0.27}Bi_{0.73}$) achieved 95% methane conversion at 1065°C in a 1.1-meter bubble column and produced pure hydrogen without CO_2 or other by-products. Under these conditions, the equilibrium conversion is 98%. When the temperature was reduced to 1040 °C, the CH_4 conversion decreased to 86%.

Steam methane (CH_4) reforming (SMR) followed by the water-gas shift reaction is the most common process for large-scale hydrogen production today. Although commercially optimized for decades, the endothermic SMR process is ex- pensive; high capital costs and high energy consumption are unavoidable. Furthermore, the process produces stoichiometric CO_2, which may impose additional costs because of the need for sequestration or because of a possible carbon tax. Despite the fundamental economic and environmental limitations of SMR, none of the presently deployed renewable power sources, including hydrogen from electrolysis, can compete with the SMR process for large-scale H_2 production.

Alternatively, H_2 can be produced by pyrolysis of CH_4 without producing CO_2 … only half as much H_2 is produced per mole of ch4 compared to SMR; however, considerably less energy input is required and solid carbon is coproduced rather than CO_2.

… Metallic catalysts (e.g., Ni, Pd, Pt) achieve high conversion and selectivity to H_2 at moderate temperatures; however, their melting temperatures are extremely high and as solids, they are rapidly deactivated by solid carbon (coke). The only report of the use of a molten metal as a catalyst for CH_4 pyrolysis described pure liquid magnesium (Mg), which was used to achieve ~30% of the equilibrium conversion, at 700 °C. Higher conversions, at higher temperatures, were not possible because of Mg evaporation.

—Upham *et al.*



Hydrogen production with a Ni-Bi molten catalyst. (A) Reactor for CH_4 conversion to H_2 and carbon in a molten-metal bubble column with continuous carbon removal. **(B)** Scanning electron microscopy image of the carbon produced. **(C)** Raman spectrum of surface carbon. The dashed line labeled "D" is at 1350 cm^{-1}, and the dashed line labeled "G" is at 1582 cm^{-1}. **(D)** Ab initio molecular dynamics simulation showing an orbital (green) of a Pt atom dissolved in molten Bi (gray) alloy. Upham *et al.* Click to enlarge.

In their study, the UCSB researchers prepared liquid alloys of active metals in low–melting-temperature metal "solvents" (Sn, Pb, Bi, In, and Ga) using known equilibrium phase behavior to produce catalysts that melt at <1000°C. The melts are used in molten-metal bubble columns, where carbon continuously floats to the surface where it can be removed.

The carbon produced—mostly graphite—accumulated as a fine powder at the top surface of the melt.

Resources

- D. Chester Upham, Vishal Agarwal, Alexander Khechfe, Zachary R. Snodgrass, Michael J. Gordon, Horia Metiu, Eric W. McFarland (2017) "Catalytic molten metals for the direct conversion of methane to hydrogen and separable carbon" *Science* 917-921 doi: 10.1126/science.aao5023

November 17, 2017 in Emissions, Hydrogen, Hydrogen Production, Natural Gas | Permalink | Comments (3)

Comments

Methane in currently plentiful and can be produced on an ongoing basis in large quantities with domestic/industrial wastes, agriculture and forestry by products etc.

Carbon is usable by many industries.

H2 could easily be stored and/or distributed to industry and for FCEVs? Would the net (H2) cost be much lower than from electrolysis?

Posted by: HarveyD | November 17, 2017 at 10:16 AM

I came across this today too:

'New CoorsTek Membrane Sciences research shows how ceramic membrane technology enables compact hydrogen generators for anyone with access to natural gas to easily and inexpensively fuel a hydrogen vehicle at home

GOLDEN, Colo.-- CoorsTek, the world's leading engineered ceramics manufacturer, today announced that a team of scientists from CoorsTek Membrane Sciences, the University of Oslo (Norway) and the Instituto de Tecnología Química (Spain) have successfully completed laboratory testing of a ceramic membrane that generates compressed hydrogen from natural gas and electricity in a one-step process with near zero energy loss. The ceramic membrane makes production of hydrogen from abundant, low-cost natural gas so efficient that it will make hydrogen the cleanest and least expensive option for future automotive fueling — surpassing both electricity and petroleum. Results of the team's breakthrough development were recently published in the prestigious peer-reviewed scientific journal Nature Energy in the research report "Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss."

The research report builds on 20 years of experience in the development and manufacturing of ceramic membranes at CoorsTek. The present membrane is made from oxides of abundant materials (including barium, zirconia, and yttrium), forming a solid ceramic electrolyte that can transport hydrogen in the form of protons at temperatures from 400 to 900 °C. By applying an electric potential over the ceramic cell, hydrogen is not only separated from other gases but also electrochemically compressed.

"Our breakthrough ceramic membrane technology makes it possible for hydrogen-fueled vehicles to have superior energy efficiency with lower greenhouse gas emissions compared to a battery electric vehicle charged with electricity from the grid," said Per Vestre, Managing Director at CoorsTek Membrane Sciences. "The potential for this technology also goes well beyond lowering the cost and environmental impact of fueling motor vehicles. With high-volume CoorsTek engineered ceramic manufacturing capabilities, we can make ceramic membranes cost-competitive with traditional energy conversion technology for both industrial-scale and smaller-scale hydrogen production."

Hydrogen is an energy carrier for next-generation fuel cell electric vehicles, and is already an important molecule for a range of industrial processes from food processing to manufacturing of glass and semiconductors, with ammonia-based fertilizers as the single largest application for hydrogen today. While a fuel cell electric vehicle will only need about 0.4 kg of hydrogen per day for typical family use, a world-scale ammonia plant needs a million times more, from 200 to 600 tons of hydrogen per day. CoorsTek Membrane Sciences research indicates that ceramic membranes can be a competitive technology for hydrogen production with integrated carbon capture, even at a scale required for cost-effective ammonia production.

"By combining an endothermic chemical reaction with an electrically operated gas separation membrane, we can create energy conversions with near zero energy loss", explains Dr. Jose Serra, Professor with Instituto de Tecnología Química (ITQ) in Valencia, Spain, a leading research lab for hydrocarbon chemistry and a co-author of the report in Nature Energy. "When you have the technology to convert energy from one form to another with almost no loss of energy, this opens up new ways to think about energy systems. For example, we can use the ceramic membrane technology to produce hydrogen from water. This will require more electric power than reforming of methane, but if electricity is available from renewable sources we can make hydrogen without CO2 emissions. You can also think one step further and design energy systems that are not only low carbon or zero carbon, but even have negative carbon emissions. This will be the case if you use renewable electricity to reform biogas to hydrogen, and store the produced carbon from the biogas underground. In this way, hydrogen can one day become a negative emission energy carrier."'

https://fuelcellsworks.com/news/breakthrough-ceramic-membrane-technology-makes-hydrogen-infrastructure-for-fuel-cell-electric-vehicl/

Until I see much fuller details, and it moves out of the lab, colour me skeptical, but it is vastly important if it works out.

Posted by: Davemart | November 17, 2017 at 01:18 PM

When and if smart affordable membranes can/could eventually separate H2 from water and/or various gas, at no or small loss with little or small CO2 emission, the H2 economy would get a major boast?

H2 production and storage facilities (of various sizes) could eventually take place in a million + places and AD-FCEVs could run 24/7 with reduced pollution and GHGs.

Posted by: HarveyD | November 17, 2017 at 06:26 PM

Post a comment

This site only allows comments from registered users. Violation of basic protocols (e.g., spoofing) will result in permanent ban. To comment, please Sign In.