Hydrogen Storage and Fuel Cells

Di-Jia Liu
Argonne National Laboratory

Short Course – Physics of Sustainable Energy
Energy Policy Institute at The University of Chicago
June 18, 2016
Global Primary Energy Supplies

Coal, 25.1%
Oil, 34.3%
Gas, 20.9%
Renewable, 13.3%
Nuclear, 6.5%

Outlook of Globe Energy Demand & its Impact to Environment

Fossil fuels will lead world energy consumption in decades to come

Energy Information Administration: [www.eia.doe.gov/iea](http://www.eia.doe.gov/iea)
IPCC Fifth Assessment 2013: [http://www.ipcc.ch/index.htm](http://www.ipcc.ch/index.htm)

GHG emission causes rise of global temperature and threatens ecosystem
U.S. National Energy Strategy

“We’ve got to invest in a serious, sustained, all-of-the-above energy strategy that develops every resource available for the 21st century.”
- President Barack Obama

“As part of an all-of-the-above energy approach, fuel cell technologies are paving the way to competitiveness in the global clean energy market and to new jobs and business creation across the country.”
- Secretary Moniz, U.S. Department of Energy

Secretary Moniz at 2015 DC Auto Show
Transportation electrification depends critically on next-generation power train development

Factors Important to Consumer

- Cost
- Durability
- Performance
- Convenience

Current Status of Polymer Electrolyte Fuel Cells and Future Direction for Development
## Different Types of Fuel Cells

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Temperature</th>
<th>Electrolyte / Ion</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane (PEM)</td>
<td>60 - 100°C</td>
<td>Nafion/H⁺</td>
<td>Electric utility, Portable power, Transportation</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>90 – 100°C</td>
<td>KOH / OH⁻</td>
<td>Military, Space</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>175 – 200°C</td>
<td>H₃PO₄ / H⁺</td>
<td>Electric utility, Distributed power, Transportation</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>600 – 1000°C</td>
<td>(Li,K,Na)₂CO₃ / CO₂⁻</td>
<td>Electric utility, Distributed power</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>600 – 1000°C</td>
<td>(Zr,Y) O₂ / O⁻</td>
<td>Electric utility, Distributed power, APUs</td>
</tr>
</tbody>
</table>

85-kW PEMFC
1.5-kW AFC
200-kW PAFC
Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Anode: \( \text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^- \)

Cathode: \( \text{O}_2 + 4 \text{e}^- + 4 \text{H}^+ \rightarrow 2 \text{H}_2\text{O} \)

Power density: 650 W/L
Efficiency: 50 to 60%
**U S DOE Fuel Cells Strategy**

<table>
<thead>
<tr>
<th>BARRIERS</th>
<th>NEAR TO MID-TERM</th>
<th>LONG-TERM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Cell Cost and Durability</td>
<td>Low-PGM catalysts, MEAs, performance durability, components</td>
<td>Non-PGM Catalysts AEMs</td>
</tr>
<tr>
<td>Hydrogen Storage</td>
<td>700 bar tanks, composites, cryo-compressed</td>
<td>Materials R&amp;D for low pressure storage</td>
</tr>
<tr>
<td>Hydrogen Production and Delivery</td>
<td>H₂ from NG/electrolysis; delivered H₂, compression</td>
<td>H₂ from renewables (PEC, biological, etc.), pipelines, low P option</td>
</tr>
</tbody>
</table>

**Level of Difficulty**
- High
- Medium
- Low to Medium

**Near and mid-term research focuses**
- Reducing platinum usage to < 0.125 g/kW (or 10 g/vehicle at 80 kW rated power)
- Increasing MEA durability to 5000 hours under cycling
- Increasing stack power density to 0.85kW/L (or stack volume of 94L for 80kW unit)
- Reducing costs of accessories, bipolar plates, air compressor, humidification, etc.

**Long-term research focuses**
- Replacing the platinum group metal (PGM) catalysts with earthly abundant materials
- Improving ion conductivity and stability of alkaline electrolyte membranes
The Electrode Catalyst Challenges - Demand for Reducing or Replacing Pt Usage

- Platinum and platinum group metals (PGMs) are catalysts of choice for polymer electrolyte fuel cell, posing a significant barrier for FCEV commercialization.

- More Pt (x3~4) is needed for cathodic oxygen reduction reaction (ORR).

- New design/synthesis and/or alternative materials are underdevelopment to reduce Pt dependence.

Data obtained from the presentation by TIAx on 80 kW direct H\textsubscript{2} PEMFC at DOE 2010 Annual Merit Review
3M’s NSTF altered conventional membrane electrode assembly morphology and significantly improved Pt usage and fuel cell performance. More need to be done in improving fuel cell robustness -
Pt Catalyst Innovation: Nanoframe Pt Alloy with Improved Activity

- PtNi nanoframe catalysts synthesized through spontaneous corrosion and annealing
- Catalysts have specific and mass activities 15 and 20x those of Pt/C
- Low-loaded MEA testing shows 3x specific activity and 2x mass activity relative to DOE targets
- Further work is needed to increase performance at high current density

Next Generation PGM-free Catalyst - Two Innovative ANL Approaches

Improving activity through rationally designed precursors – MOFs/POPs

*Volumetric Activity* $\propto$ *Turn-Over-Freq.* $\times$ *Site Density*

• Argonne introduced Metal-organic-framework & porous organic polymer as next-generation catalyst precursors
• “Support-free” and pore-former free
• Uniform distribution & high active site density

Improving mass/charge transports through nanofibrous network

• Argonne’s nano-fibrous network provides higher surface area and nearly exclusive micropores
• New electrode offers enhanced mass transport and charge transfer via a unique micro-macro-porous nano-network

Conventional

New ANL design

Conventional

ANL nano-network

New 3-D precursors breaks away from 50-years of square-planar molecular approach

New nano-network architecture not only increases surface area but also site density
“One-Pot” Synthesis of MOF-based TM/N/C Catalysts

Mixing

Organic Ligands + ZnO

Different MOFs

TM/N/C Catalysts

Thermolysis

P = 924 mW/cm² @ 0.38V

P = 855 mW/cm² @ 0.47V

Catalytic Mass/Charge Transport Improvement through Nanonetwork Architecture

Conventional Support

- Impeded $O_2$ transport through porous carbon, macro $\rightarrow$ meso $\rightarrow$ micro
- Hindered charge transfer through particle percolation
- Exposed active site at carbon surface

Nanofibrous Support

- Improved $O_2$ transport through voids b/w fibers, macro $\rightarrow$ micro
- Enhanced charge transfer via fiber nanonetwork
- Embedded catalytic site inside nanofibers
ANL’s PGM-free Catalyst with Nano-network Architecture

Fabrication of PGM-free catalyst with nano-network architecture

Electrospinning

Conversion to catalyst

Fuel cell fabrication


Comparison of PGM-free nano-network catalyst (Fe/N/CF) with Pt/C
Current Status of On-board Hydrogen Storage and Future Direction for Development
Opportunities & Challenges in Hydrogen Storage for Transportation Application

**Onboard H₂ production**
- Catalytic reforming of hydrocarbon fuels
- Existing fuel distribution network
- Start up time
- System efficiency (fuel utilization & CO₂ reduction)

**Onboard H₂ storage**
- Compressed hydrogen
- Different storage media (chemical, metallic, carbon-based, etc)
- Needs H₂ distribution infrastructure
- Storage capacity issues

---

**DOE System Targets for On-Board Hydrogen Storage for Light-Duty Vehicles**

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric</td>
<td>kWh/kg</td>
<td>1.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Capacity</td>
<td>(kg H₂/kg system)</td>
<td>(0.055)</td>
<td>(0.075)</td>
</tr>
<tr>
<td>System Volumetric</td>
<td>kWh/L</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Capacity</td>
<td>(kg H₂/L system)</td>
<td>(0.040)</td>
<td>(0.070)</td>
</tr>
</tbody>
</table>
DOE Technology Portfolio of On-board H₂ Storage

**Dual approach**

- **Near-Term Approach**
  - 700 bar Compressed
  - Cold / Cryo-Compressed
  - Metal Hydrides
  - Sorbents
  - Chemical H₂ Storage

- **Longer-Term Approach**

**Technology Focus**

- 700 bar Compressed
- Cold / Cryo-Compressed
- Metal Hydrides
- Sorbents
- Chemical H₂ Storage

**Barriers and R&D Focus**

- **Near-Term Approach**
  - Lower Cost Carbon Fiber
  - Improved Composites
  - Conformable designs
  - Lower Cost BOP
  - System Engineering
  - Advanced Insulation
  - Improved Dormancy
  - Composite Development

- **Longer-Term Approach**
  - Higher Material Capacity
  - System Cost
  - Fill Time
  - Onboard Efficiency
  - Higher Material Capacity
  - System Cost
  - Dormancy
  - WTP Efficiency
  - Lower Cost Off-board Regen
  - System Cost
  - Gravimetric Density

---

The long term objective is a vehicle with a range of at least 300 miles
Current Status of Hydrogen Storage Technology

**KEY CHALLENGE:** >300-mile driving range in all vehicle platforms, without compromising passenger/cargo space, performance, or cost

![Graph showing various hydrogen storage technologies and their capacities.](image)

- **Gravimetric Capacity (wt%)**
- **Volumetric Capacity (g/L)**

- **C-sorbent**
- **Alane Slurry**
- **MOF-177 (250 bar)**
- **Complex hydride**
- **Chemical hydride**
- **Cryocompressed**
- **Liquid hydrogen**

- **Revised DOE system targets**
- **2015 Ultimate**

Source: US DoE, Fuel Cell Technologies Program
# Low Pressure H₂ Storage Material Challenges

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Examples</th>
<th>Advantages</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Hydride</td>
<td>LiBH₄, NaBH₄, Mg(BH₄)₂, etc.</td>
<td>High volumetric &amp; gravimetric capacities, Highly stable at ambient temperature</td>
<td>Discharge-charge kinetics &amp; time, Reversibility, Parasitic energy consumption</td>
</tr>
<tr>
<td>Chemical Hydride</td>
<td>NH₃-BH₃, C₆H₅-CH₃, etc.</td>
<td>Good gravimetric &amp; volumetric capacities, Stable at ambient temperature</td>
<td>Poor on-board/off-board regen, Parasitic energy consumption</td>
</tr>
<tr>
<td>Sorbent</td>
<td>MOF, POP, Porous carbon, etc.</td>
<td>Good gravimetric capacity, Fast discharge-charge time and lower energy consumption</td>
<td>Cryo-compression needed, Unstable at ambient temperature (dormancy concern)</td>
</tr>
</tbody>
</table>

- Low pressure storage is essential in improving overall system efficiency
- Fundamental understanding and molecular manipulation are critical in advancing next-generation storage materials
Sorption-based Material Challenges: Some Examples of Next-generation Adsorbent Approaches

Metal-O rganic Framework (MOF) Sorbents

- Design of high surface area & narrow/adjustable pore size
- Incorporating “metallic” feature
- Develop fundamental understanding through modeling and advanced characterization

Porous Organic Polymer (POP) Sorbents

- Improving storage capacity and H₂ binding energy through molecular design

Improving storage capacity and H₂ binding energy through molecular design
Improving H₂ Discharge-Charge Reversibility using Graphene Encapsulated Hydride

\[
\text{NaBH}_4 \leftrightarrow \text{Na} + \text{B} + \text{H}_2, (\text{B}_2\text{H}_6, \text{etc.})
\]

“Graphene wrapping” prevents the escape of dehydrogenation products and catalyzes the rehydrogenation during H₂ charging.


More innovative approaches combined with improved fundamental understanding could ultimately resolve the current issues in H₂ storage!
Hydrogen Production and Distribution Infrastructure Development
Borrow a Page from Gasoline Distribution?
DOE’s H₂ Production & Delivery RD&D Portfolio

US DOE – Fuel Cell Technologies Office
H₂ Infrastructure Development and Status

Nationwide

- 1,500 mi. of H₂ pipeline
- >9M metric tons produced/yr
- ~50 stations (~10 public)

California

- >~$70M awarded
- ~$100M planned through 2023
- Goal - 100 stations

Other States

- 8-State MOU Members: CA, CT, NY, MA, MD, OR, RI and VT
- MA, NY, CT: Preliminary plans for H₂ infrastructure and FCEVs deployment in metro centers in NE states.
- Hawai‘i: Public access refueling infrastructure on Oahu by 2020

NE states, California, and Hawaii have H₂ infrastructure efforts underway
Representative Hydrogen Refueling Stations

DTE/BP Power Park, Southfield, MI

LAX refueling station

Hydrogen and gasoline station, WA DC

Chino, CA

Courtesy K. Wipke, National Renewable Energy Laboratory and the California Fuel Cell Partnership
H₂ at Scale - A “Big Idea”
Major Administration Energy Goals

1. Reduce GHG emissions by 17% by 2020, 26-28% by 2025 and 83% by 2050 from 2005 baseline

2. Reduce net oil imports by half by 2020 from a 2008 baseline

3. Double energy productivity by 2030

4. By 2035, generate 80% of electricity from a diverse set of clean energy resources

5. Reduce CO₂ emissions by 3 billion metric tons cumulatively by 2030 through efficiency standards set between 2009 and 2016

H₂ at Scale primary impact on 1 and 4 (above), also impacts 2.
Energy System Challenges

- Multi-sector requirements
  - Transportation
  - Industrial
  - Grid

- Renewable challenges
  - Variable
  - Concurrent generation

Over half of U.S. CO₂ emissions come from the industrial and transportation sectors

Denholm et al. 2008
Carbon-free Electricity Prices Continually Drop with Increase in Capacity

Source
(Arun Majumdar)
1. DOE EERE
Sunshot Q1’15 Report
2. DOE EERE
Wind Report, 2015
Conceptual H$_2$ at Scale Energy System

*Illustrative example, not comprehensive*
BAU (Business As Usual) vs. High H₂ - CO₂ Difference

Emissions difference between 2050 high-H₂ and AEO 2040 scenarios (million MT)

Red flows represent a reduction (between scenarios)

45% reduction in CO₂ emissions
Grid 75%, Transportation 25%, Industrial 25%
Acknowledgement

- Fuel Cell Research - Shengqian Ma, Dan Zhao, Shengwen Yuan, Jianglan Shui, Gabriel Goenaga, Chen Chen, Heather Barkholtz, Lina Chong, Lauran Grabstanowicz, Alex Mason, Brianna Reprogle, Sean Comment, Zachary Kaiser, Junbing Yang, Debbie Myers

- Technology & Implementation Analyses - John Kopasz, Tom Benjamin, Nancy Garland

- H2 at Scale – Amgad Elgowainy

- DOE Program Managers – Nancy Garland, Dimitrios Papageorgopoulos