Surface technology should improve PEM fuel cell performance

Live Mølmen[1,~~2~~], Anna Alexandersson[1], Peter Leisner[1,2]

1) RISE Research Institute of Sweden, Borås/Lund, Sweden
2) School of Engineering, Jönköping University, Jönköping

Electrification is the main solution in the transition to a sustainable society independent of fossil resources. However, it is a serious challenge to find appropriate energy storage solutions. Even though, battery technology is in strong development, it is not a cost and resource efficient solution for large scale and long term energy storage; even for mobile applications batteries have limits. The solution for several leading industrial nations is to invest in hydrogen as energy storage solution with fuel cells as the main converter to electric energy.

The Fukushima catastrophe resulted in a complete change in the Japanese energy policy. In 2017, Prime Minister Abe declared that Japan will be ~~the~~ first in the world to realize a hydrogen-based society. This was soon followed by a national strategy for full-scale hydrogen supply and hydrogen-based power supply. Furthermore, leading Japanese car manufactures, energy companies and investors have formed the consortium 'Japan H_2 Mobility' with the purpose to make Japan leading in automotive hydrogen solutions [1]. A similar development is going on in Germany where the government decided on 'Energiwende' in 2011 [2], also as a consequence of Fukushima. The transport sector is going to be electrified and all major car manufactures are in the process of offering fuel cell cars. Both Japan and Germany present strong coordination between political decisions, industrial investments and academic research programmes. Also in China, is the development of fuel cell vehicles under development and could soon represent the largest investment in the world [3].

Even though, the USA is far from being able to present similar coordinated actions on federal level, there are some strong points. The Department of Energy has for many years supported introduction of fuel cell forklift trucks, resulting in more than 21~~0~~~~11~~ 000 trucks sold [4~~X~~], mainly for central warehouses, where they have performed well in total cost of ownership analysis [5~~Y~~]. Nikola Motor Co will soon start volume production of fuel cell powered semi-trucks with performance competing with conventional combustions engine alternatives. In parallel, they will build ~~an~~ their own infrastructure for hydrogen refuelling in USA and Canada. Finally, California has since the 70's developed own high standards for environmental durability as an inspiration for many other states. It is worth to notice that if California had been an independent state it, would had been the eighth largest economy in the world.

Development challenges

Materials development is still needed to meet these serious goals for common use of fuel cells in a cost efficient way.

There are several different types of fuel cells, differing both in the fuel, mainly methanol or hydrogen gas, and in the electrolyte and electrodes used in the cell. The fuel cells that were first commercialized used an aqueous alkaline electrolyte. Later, the polymer electrolyte membrane

(PEM) fuel cell was developed and is now dominating the commercial market~~the dominating type~~. Since the polymer acts as both separator and electrolyte, there is no aqueous phase except the flow of produced water. These cells are therefore more mechanically stable and can even be operated at elevated pressure. Furthermore, there are also solid oxide electrolyte fuel cells. These have higher efficiency, but also require temperatures ~~over~~ above 600 °C to increase the proton conductivity of the oxide.

For use in mobile applications, the fuel cell must be both compact and lightweight. Additionally, there are strict safety requirements that need to be met. The alkaline fuel cell is generally too heavy and too large to be used in mobile application, while the high temperature of the SOFC is unsuitable due to safety precautions. PEM fuel cells are therefore in focus for mobile applications.

The Hydrogen Technology Challenging Programme under the International Energy Agency (IEA) has defined the three most important areas for material development to reduce the cost of PEM (polymer electrode membranes) fuel cells for mass-market introduction to be [64]:

1) High-performance electrode catalyst enabling ultra-low precious metal loading,
2) Low cost, lighter and corrosion resistant bipolar plates,
3) Low cost, high-performance polymer electrolyte membrane.

The PEM fuel cell

The central part of the fuel cell is the polymer electrolyte membrane (Figure 1). The membrane is made of a perfluorinated sulfonic acid polymer (PFSA) and is chosen due to it being electrically isolating, but at the same time proton conductive. Furthermore, it is often reinforced so that it is also mechanically stable, and can sustain elevated pressures, and even differential pressure between the anode and cathode side of the cell.

In theory, the chemical energy from the fuels can be extracted as long as there is an ion conductive separator and an external circuit present. However, the reactions are slow, and a catalyst is needed. The most common catalyst ~~in the PEM fuel cell~~ is Pt nanoparticles. The particles are supported on a conductive substrate, usually carbon black. To be functional, it is essential that the catalytic particles are located at triple phase boundaries where the electrode meets the PEM and the gas (hydrogen at the anode and oxygen at the cathode).

The catalyst is most often produced by depositing Pt nanoparticles onto the carbon support. Often, an ink is made of the Pt/C, ionomer and a solvent. The ionomer is added to ensure proton transport throughout the catalyst layer. The ink can be coated onto the PEM or the gas diffusion layer (GDL) by spraying, decal, brushing or other methods before it is dried, leaving a porous structure with the catalyst, catalyst support, and ionomer all in contact [~~5~~7,8~~6~~].

Bipolar plates are made of either graphite or stainless steel. Graphite tends to be bulky and has less as good mechanical stability. Stainless steel, on the other hand, is not stable enough in the corrosive environment of the fuel cell, and requires a protective coating, which increase the price of the bipolar plates. The main functions of the bipolar plates are to be current collectors and to distribute the gasses in the cell.

To ensure electrical contact as well as mass flow to the catalyst layer, the GDL is added as a conductive porous material between the bipolar plate and the catalyst layer. The GDL is most often made of carbon, either carbon felt or paper, as this is cost efficient and sufficiently stable against corrosion not to be limiting for the lifetime [9~~7~~].

Degradation issues in the PEM fuel cell

~~-~~As mentioned above, the environment inside a PEMFC is highly corrosive. Especially the cathod~~ic~~e side that has both oxygen and water readily available for the fuel cell reaction, and the anode side during start-up and shut-down, as oxygen generally has diffused into the anode compartment during the period of downtime, and potential reversal might occur. Furthermore, the elevated temperature, acidic environment due to the low pH of the membrane and the potential over the cell further destabilizes the materials used.

For the bipolar plates, graphite has proven to be sufficiently electrochemically stable. However, due to its brittle nature graphite bipolar plates are thicker ~~to~~ than ~~the~~ metallic counterparts.

Stainless steel has been the most promising materials due to formability and cost. However, stainless steel is not corrosion resistant in the PEM fuel cell, and protective coatings must be added. These coatings are mainly nitrides [~~8~~10], carbides or conductive polymers for commercial applications, while some research projects even utilizes platinum to ensure high conductivity. Research is being conducted on lighter metals for use in the bipolar plates. Titanium has been studied as it is lighter than steel. However, the naturally formed titanium oxide layer that passivates and protects the titanium from further corrosion is also electrically insulating, and the surface must thereby still be coated to decrease the contact resistance~~remain conductive~~. Another alternative metal is aluminum, but also here research is conducted to find appropriate surface coatings to protect the metal from corrosion [11~~9~~].

The membrane is one of the parts of the fuel cell that is easily degraded. It is very sensitive to impurities. Metal cations present in the cell due to corrosion of the bipolar plate can migrate into the membrane and block the proton conductive sites. Furthermore, pinholes can occur due to mechanical stress, and degradation will increase in so-called hot-spots that are formed due to heterogeneous current distribution on the surface [12~~0~~].

The catalyst layer degrades in two main ways. Firstly, the Pt nano-particles, dissolve, and platinum ions migrate into the membrane, or agglomerate to lager particles through Ostwald ripening. The ions that migrate into the membrane reacts with hydrogen and redeposit as Pt particles inside the membrane. However, as these are not in contact with the GDL, they are no longer electrocatalytically active [12~~0~~,1~~1~~3]. Secondly, also the carbon support material corrodes, partially because Pt also catalyzes the carbon corrosion reaction. When the carbon support is corroded, the Pt nanoparticles detach and lose the electrical contact [14~~2~~]. Additionally, the porous structure collapses so that the flow of reactants and products is reduced [~~7~~9]. ~~Ongoing research focuses on electrodeposition of Pt alloy nano-particles where alloying with Ni and Co is investigated to improve the long term efficiency of the catalysts [13].~~ Ongoing research focuses on reducing the amount of Pt required and improving the long term efficiency of the catalysts. This is done by different deposition techniques like electrodeposition, and alloying with other elements, e.g. Ni and Co [15~~3~~].

In summary, the PEM fuel cell is a complex system with several materials in contact. Furthermore, the high temperature, humidity and acidic environment set high requirements for the corrosion resistance of the materials that are used. Surface technology plays a key role in the development of cost efficient and durable PEM fuel cells.

Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 764977.

References

1. //www.jhym.co.jp/en/ (accessed 2019-03-09)

2. W. Paatsch, Energy turnaround – a challenge for surface technology, TIMF 94, 5 (2016) 228-230

3. H. Sanderson, Hydrogen power: China backs fuel cell technology, Financial Times Collections, Energy and the future, January 2, 2019.

4~~X~~. P. Devlin, G. Moreland, Industry Deployed Fuel Cell Powered Lift Trucks, DOE Hydrogen and Fuel Cells Program Record 18002, 5/30/2018

5~~Y~~. T. Ramsden, An Evaluation ot the Total Cost of Ownwership of Fuel Cell Powered Material Handling Equipment, Technical Report NREL/TP-5600-56408, National Renewable Energy Laboratory, April 2013

6~~4~~. Hydrogen Tracking Clean Energy Progress, IEA, 7 August 2018, //www.iea.org/tcep/energyintegration/hydrogen/

7~~5~~. H. Park, S. Choe,H. Kim, D-K. Kim, G. Cho, Y. Park, Direct fabrication of gas diffusion cathode by pulse electrodeposition for proton exchange membrane water electrolysis. Appl Surf Sci. 2018, ~~;~~**444**, ~~:~~303–311

8~~6~~. S. Khandavalli, J.H. Park, N.N. Kariuki, D.J. Myers, J.J. Stickel, K. Hurst, Rheological Investigation on the Microstructure of Fuel Cell Catalyst Inks. ACS Appl Mater Interfaces. 2018, ~~Dec 19;~~**10**, (50), ~~:~~43610–43622

9~~7~~. H. Liu, M.G. George, N. Ge, D. Muirhead, P. Shrestha, J. Lee, Microporous Layer Degradation in Polymer Electrolyte Membrane Fuel Cells. J Electrochem Soc. 2018, ~~Jan 1;~~**165**, (6), ~~:~~F3271–F3280

10~~8~~. S. Pugal Mani, A. Srinivasan, N. Rajendran, Effect of nitrides on the corrosion behaviour of 316L SS bipolar plates for Proton Exchange Membrane Fuel Cell (PEMFC). Int J Hydrog Energy. 2015, ~~Mar 2;~~**40**, (8), ~~:~~3359–3369

11~~9~~. M.A. Deyab, Corrosion protection of aluminum bipolar plates with polyaniline coating containing carbon nanotubes in acidic medium inside the polymer electrolyte membrane fuel cell. J Power Sources. 2014~~ Dec 5~~, ~~;~~**268**, ~~:~~50–55

12~~0~~. L. Dubau, L. Castanheira, F. Maillard, M. Chatenet, O. Lottin, G. Maranzana, A review of PEM fuel cell durability: materials degradation, local heterogeneities of aging and possible mitigation strategies. Wiley Interdiscip Rev Energy Environ. 2014~~;~~, **3**, (6), ~~:~~540–560.

1~~1~~3. N. Yousfi-Steiner, P. Moçotéguy, D. Candusso, D. Hissel, A review on polymer electrolyte membrane fuel cell catalyst degradation and starvation issues: Causes, consequences and diagnostic for mitigation. J Power Sources. 2009, ~~;~~**194**, (1), ~~:~~130–145.

14~~2~~. N. Mansor, T.S. Miller, I. Dedigama, A.B. Jorge, J. Jia, V. Brázdová, Graphitic Carbon Nitride as a Catalyst Support in Fuel Cells and Electrolyzers. Electrochimica Acta. 2016, ~~;~~**222**, ~~:~~44–57

15~~3~~. A. Egetenmeyer, M. Baumgärtner, T. Linckh, D. Durneate, H. Natter, R. Hempelmann, I. Radev, V. Peinecke, Pulse electrodeposition of catalyst nanoparticles for application in PEM fuel cells, 2017, **25**, (1), 9-19.~~-~~

Formatted: Normal

Formatted: Indent: Left: 0 cm, Hanging: 0,75 cm

Formatted: English (United States)

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font: Bold

Formatted: Font: Bold

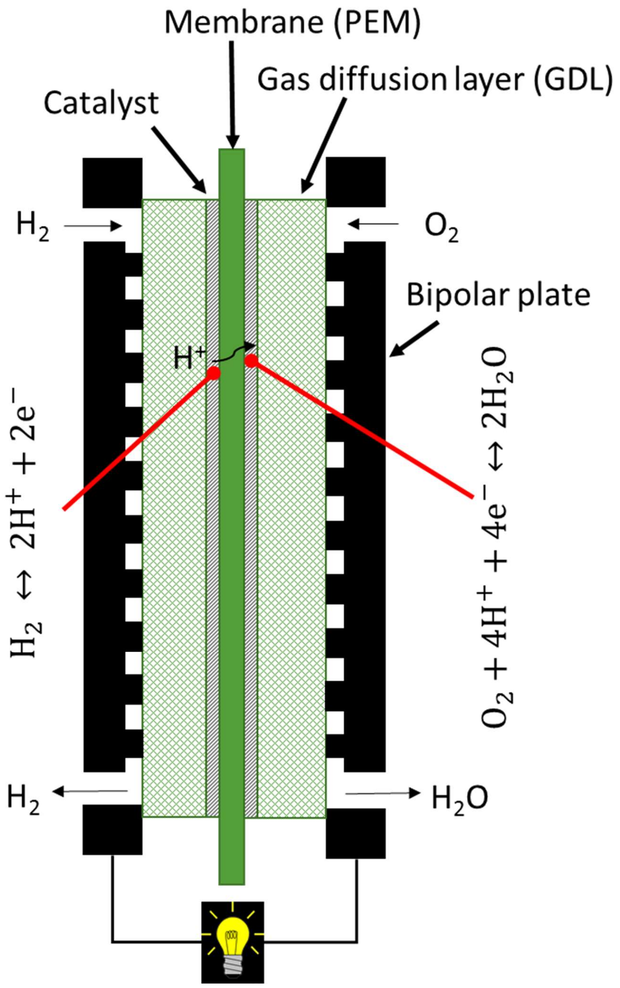

Figure 1: Sketch of the cross-section of a PEM fuel cell. Cells are stacked, making one side of the bipolar plates connected to the anode in one cell and the other side to the cathode of the next cell. Therefore, it is called a bipolar plate.