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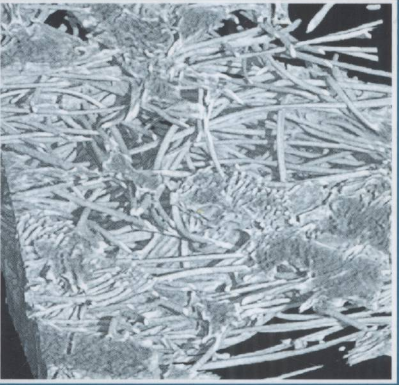

Materials for fuel cells

Edited by Michael Gasik

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Materials for fuel cells

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Contents

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Introduction: materials challenges in fuel cells

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1.1 What is a fuel cell?

A fuel cell is an electrochemical device that converts the chemical energy of a reaction (between fuel and oxidant) directly into electrical energy. The basic physical structure, or building block, of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side [1]. In a typical fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) and an oxidant (i.e. oxygen from air) is fed continuously to the cathode (positive electrode); the electrochemical reactions take place at the electrodes to produce an electric current. A fuel cell should not be confused with secondary batteries (accumulators). The battery (primary) is an energy storage device. The maximum energy available is determined by the amount of chemical reactant stored within the battery itself. The battery will cease to produce electrical energy when the chemical reactants are consumed (i.e. discharged). In a secondary battery, the reactants are regenerated by recharging, which involves putting energy into the battery from an external (electricity) source. The fuel cell, on the other hand, is an energy conversion device that theoretically has the capability of producing electrical energy for as long as fuel and oxidant are supplied to the electrodes [1, 2].

The history of the fuel cell principle dates back to 1839, when Sir William Grove made his famous invention [3, 4]. That fuel cell was in fact the earliest version of a lead-acid accumulator, but it employed platinum electrodes with sulphuric acid electrolyte. Platinum here was seemingly working as both a catalyst and a current collector. However, Grove did consider a fuel cell not as a primary source of power but rather a method "effecting the decomposition of water by means of its composition" [3]. Initially, fuel cells were seen as an attractive means for the generation of power because the efficiencies of other technologies were very poor. For instance, the coal-burning generation station built by T. Edison in Manhattan in 1882 converted only about 2.5% of the available energy into electricity. W. Ostwald has written in his visionary paper about the wastefulness of steam engines already in 1894 and expressed his hope that the next century would become the "Age of Electrochemical Combustion" [5]. Still in the 1920s the overall thermodynamic efficiency of reciprocating steam engines was approximately 13–14%, and steam turbines obtained just under 20%. These poor thermal efficiencies provided one of the major motivations for the pioneers of fuel cell development [4]. Because of the role of coal as the major fuel at the beginning of the 20th century, the emphasis was put on coal-derived fuels first. One of the pioneering works was done by L. Mond (founder of INCO) and C. Langer to develop a coal gasification process producing a hydrogen-rich gas [4, 6]. At that time, however, sulphur and other impurities in the gas resulted in fast poisoning of platinum catalysts and thus high costs of the fuel cells' energy. As the efficiency of other technologies rapidly improved, the interest in fuel cells waned. Only when the "space race" began in the late 1950s were fuel cells rapidly developed for deployment in space [2, 4].

1.2 Why fuel cells?

Today (and likely still tomorrow) increased energy and power generation demand is being met largely by reserves of fossil fuel that emit both greenhouse gases and other pollutants. Those reserves are diminishing and they will become increasingly expensive [7]. Currently, the level of CO_2 emissions per capita for developing nations is 20% of that for the major industrial nations. As developing nations industrialise, this will increase substantially. By 2030, CO_2 emissions from developing nations could account for more than half the world's CO_2 emissions. These emissions, however, could be substantially reduced, even if hydrogen is derived from fossil fuels, due to the much higher efficiency of fuel cells [2].

The efficiency of a fuel cell (besides absence of moving parts, noise and less emissions) has been the most attractive feature since their invention – unlike a heat engine, the fuel cell does not need to achieve the large temperature differential to achieve the same Carnot cycle efficiency as the heat engine. This is because of the added energy gained from Gibbs free energy as opposed to simply the thermal energy – the theoretical efficiency limit for a fuel cell is thus simply $\Delta G^\circ / \Delta H^\circ = 1 - T \cdot \Delta S^\circ / \Delta H^\circ$. For hydrogen oxidation into water this value is about 80–90% depending on temperature and pressure. The resulting freedom from large temperature differentials in the fuel cell provides a great benefit because it relaxes material temperature problems when trying to achieve comparable efficiency [1].

1.3 Which fuel cell?

A variety of different fuel cell types exist classified by use of diverse categories, depending on the combination of type of fuel and oxidant, whether the fuel is processed outside (external reforming) or inside (internal reforming) the fuel cell, the type of electrolyte, the temperature of operation, whether the reactants are fed to the cell by internal or external manifolds, etc. [1]. Theoretically, any substance capable of chemical oxidation that can be supplied continuously (as a fluid) can be "burned galvanically" as fuel at the anode of a fuel cell. Similarly, the oxidant can be any fluid that can be reduced at a sufficient rate. Gaseous hydrogen has become the fuel of choice for most applications, because of its high reactivity when suitable catalysts are used, its ability to be produced from hydrocarbons for terrestrial applications, and its high energy density when stored cryogenically for closed environment applications, such as in space. Similarly, the most common oxidant is gaseous oxygen, which is readily and economically available from air for terrestrial applications, and again easily stored in a closed environment [1]. The most common classification of fuel cells is by the type of electrolyte used. It includes:

1. polymer electrolyte fuel cell (PEFC), also known as proton exchange membrane (PEM) fuel cell
2. alkaline fuel cell (AFC)
3. phosphoric acid fuel cell (PAFC)
4. molten carbonate fuel cell (MCFC), and
5. solid oxide fuel cell (SOFC) [1, 2].

PEM fuel cells may also use methanol as a fuel so these fuel cells are often called also "direct methanol fuel cells" (DMFC). "Direct" means that fuel (methanol in this case) is not being externally reformed in any way, but rather oxidised directly. It is clear that the operating temperature, and useful life and power density of a fuel cell dictate the physicochemical, thermomechanical and other properties of materials used in the components (i.e., electrodes, electrolyte, interconnect, current collector, etc.).

1.4 Fuel cells and materials challenges

Fuel cells thus are demonstrating excellent efficiency, high reliability and low emissions. Why are they not yet in our everyday use? Since their invention, fuel cell deployment has been hindered by several major technical factors: high costs of basic elements and materials, uncertain long-term stability of the components, sensitivity to different poisons present in fuels (SO_2, CO, H_2S, NaCl, etc.). Independently of fuel cell types, costs have been the major drawback, raising the fuel cell electricity costs far beyond "conventional" electricity prices despite higher efficiency values. More efficient membranes, electrodes, and catalysts are continually being developed. It is becoming clear that the success of fuel cells will be mainly based on the ability of industry to offer cheaper and better materials: catalysts without noble metals, new carbon materials, novel electrolytes and membranes, reliable interconnect materials, etc.

Materials challenges for fuel cells are very demanding. In this book only some of the examples will be shown to demonstrate the multifunctionality of the fuel cells environment and the multi-science approach one should use to find proper solutions. Different fuel cell types present different demands for materials combinations and their working conditions. Different applications employ additional constraints. For instance, for fuel cell electrical vehicles (FCEV) current limitations for extreme operating conditions are based on the properties of the materials used in current FCEV prototypes. Increasing the power of a fuel cell stack thus corresponds linearly to increased use of materials like, for example, platinum in the catalyst and weight and volume of the stack. Catalysts are one of the key materials in fuel cells in respect of both performance and costs. It is known that the best catalytic activity in fuel cells reactions is provided by noble metals like platinum, palladium, etc. Unfortunately, extensive use of noble metals is cost-prohibitive – if one considers the US car fleet shifting towards fuel cell vehicles, worldwide platinum and palladium recovery should be increased by at least for 48% at current price levels. It is unlikely that substantial noble metal mining would increase so, and a significant (a few times) price reduction would be expected. Thus, fuel cells must employ alternative catalysts with less noble metals [1, 8–11]. Car manufacturers have noted that strategies have to be developed to increase the specific power density of fuel cells stacks with minimum loss in cell efficiency. New catalysts, oxidant enrichment technologies and catalytic activity increasing are the major directions.

As authors [9] point out, it is of note, that materials presently being used in PEMFC and SOFC are essentially the same as those that were suggested in the 1980s. Despite innovative fabrication processes and materials tailoring, only in the last few years have engineering and commercialisation issues highlighted the inadequacies of originally chosen materials [9].

1.5 Structure of the book

Fuel cells have already been proven to have excellent efficiency versus other means of power generation. The major obstacles seen during the last few years concern cost, long-term durability and service issues. For any material, performance, manufacturing and applications are essential issues. Today, more than ever, the global community can see that the predictions of Jules Verne may finally come to reality. He wrote: “I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable” (“The Mysterious Island”, 1874). To take a small step towards this vision, the authors of this book have made