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PROJECT SUMMARY NO PS229

Novel Materials Process for Alcohol Based Fuel Cells

OBJECTIVES

- To produce cheap alcohol based fuel cells through the development of two novel types of material, and the development of alternative production techniques and catalysts.
- Test these fuel cells in conditions typical of small electronic devices (room temperature, low flow rates) and achieve a lower cost per kW output that the current Industry standard (Nafion).

SUMMARY

ITM Power Plc, working with Cranfield University, have developed cheap novel ion permeable membranes for use in alcohol fuel cells. These are based on hydrophilic polymers and radiation grafted hydrocarbon polymers, and each has been formulated to allow either cation exchange (CE) or anion exchange (AE). These chemistries have been refined, tested in fuel cells at room temperature and compared to Nafion 117, the current industry standard.

For the newly developed CE systems, the hydrophilic membranes cost £316/kW, the radiation grafted membranes cost £950/kW, both of which compare favourably to Nafion 117 membranes at £1815/kW.

For the AE systems, the membrane cost per unit area is comparable to the CE systems, however, power density is reduced as a result of lower catalytic activity from the Pt based catalysts, resulting in higher costs per unit power. In spite of this increase in cost per unit power, the use of AE systems may still offer considerable advantage over the CE systems, as non-platinum catalysts can be used, which offer a cost benefit without serious detriment to the power output.

In addition, this project has shown that the use of a liquid oxidant offers considerable improvements in power outputs, therefore further reducing cost per unit power.

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COST

The total cost of the project, £469,250, is being met by the Department of Trade and Industry (DTI).

DURATION

53 months – 01 April 2001 to 31 August 2005.

BACKGROUND

This report is the summation of a development programme conducted by ITM Power Plc, in conjunction with Cranfield University, to develop cheap novel materials and processes for alcohol based fuel cells. These devices are of commercial interest as they offer the prospect of power sources with a high efficiency, high energy density and rapid refuelling times for a range of electronic devices such as mobile phones, laptops and MP3 players. The market for such fuel cells is estimated to be worth $800 million by 2010[1].

At present, the key reason for the poor sales of fuel cells is their unit cost. This is due to the price of two key components:

- The ion exchange membrane, which separates the fuel and oxidant. Currently, the market is dominated by Nafion™, a product developed by DuPont, for which the cheapest available price is ~£270/m^2 ($500/m^2). This is an acidic membrane which separates the fuel and oxidant, but is permeable to hydrogen ions (protons).
- The catalyst. This is invariably made from platinum, which is currently trading for £15,250/kg on the commodity markets. Despite its high cost, for alcohol fuels, this is the most effective catalyst for the acidic chemistry of Nafion.

The majority of companies working to develop fuel cells use Nafion, and hence platinum. The only realistic way they can reduce the unit cost of their fuel cells is to try to increase the power output per cm^2 of membrane (and hence per gram of catalyst). Many papers and research projects have been dedicated to increasing their power density with the general conclusion that it can only be achieved through working at elevated temperatures (~70°C) and high fuel / oxidant pressures and flow rates. Unfortunately, these working conditions are not suitable for the small portable device market for which the fuel cells are developed.

During this project, ITM Power have sought to take a fresh approach to the problem by developing two new categories of cheaper ion exchange membranes; thus negating the requirement for Nafion. The membranes developed at ITM are based on ionic hydrophilic polymers, made by bulk co-polymerisation from solution, (henceforth referred to as 'Type 1' polymers), while Cranfield

1 World Fuel Cells- An Industry Profile with Market Prospects to 2010, Elsevier Advanced Technology, 2002

University have been contracted for their expertise in imparting polymers with ionic properties through radiation grafting (henceforth referred to as ‘Type 2’ polymers). By approaching the problem through the development of two distinct novel ion permeable membranes, the company sought to increase the chance of project success, while expanding its suite of materials.

During the project, each type of conductive polymer was developed as both acidic (with similar chemistry to Nafion) and alkaline based membranes. The latter have the potential to use cheaper catalysts than platinum, creating a further cost saving.

THE WORK PROGRAMME

Before the project, versions of the Type 1 and Type 2 CE technologies had been developed for use with hydrogen. Thus, considerable alteration of these chemistries, plus complete formulation of the AE membranes were required. The resulting membrane chemistries were assessed through measurement of membrane ionic conductivity and fuel permeability. For Type 1 and Type 2 technologies, CE membranes were found to have conductivities of 2.25 and 2.44 times that of Nafion 117, while the AE membranes had values of 1.42 and 3.63 times that of alkaline conditioned Nafion 117. An additional commonly used comparator between membranes is the ratio of conductivity to methanol crossover, although ITM have been unable to confirm or define how this related to fuel cell performance. The best AE and CE ratios are 7.9 and 16.5 times that of Nafion 117.

From this data, a total of four materials were tested as methanol fuel cells; an AE and a CE material of each ion permeable membrane technology. These were compared to the performance of commercial Nafion 117 AE[2] and CE materials. For reasons of reproducibility, the catalyst selected for the comparison was commercial Pt and Pt-Ru loaded carbon cloths, and they were tested using a variety of methanol concentrations at room temperature. The performance was assessed by conducting a series of polarisations and noting the peak power during polarisation. As this is a commercial project, for comparison reasons, results were calculated as membrane £/kW at this peak power, MEA £/kW was only used when different catalyst systems were compared.

It was found that for CE materials, the cheapest membrane per kW output was the Type 1 membrane at £316/kW, compared to Nafion at £1815/kW. See Figure 1. For AE materials, the Type 1 membrane was again the cheapest at £1019/kW, compared with Nafion 117 AE at £6923/kW. See Figure 2.

2 No commercially available anion exchange material is available. Thus, ‘Nafion AE’ is made by conditioning Nafion 117 in an alkaline environment.

It was considered that as the Type 1 membranes were up to 20 times thicker than the Nafion and Type 2 membranes, the development of thin Type 1 membranes should result in significant increases in power.

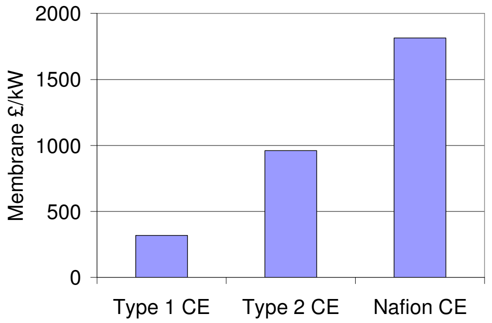

Figure 1. Comparing the cost per kW for different CE membranes.

Tests were also conducted into the use of palladium (Pd) as a cheaper alternative catalyst to platinum (Pt). It was found that palladium had a lower MEA £/kW than Pt when used on the fuel side of the cell. Furthermore, the addition of a liquid oxidant to a Pd cell further reduced the MEA £/kW compared with oxygen.

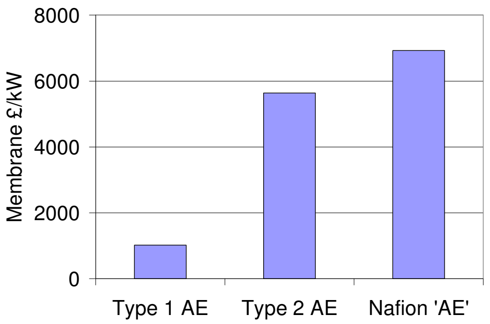

Figure 2. Comparing the cost per kW for different AE membranes.

A further test was conducted using ITM's patented 'One-Shot' process, in which the Membrane Electrode Assembly (MEA) is created in a single polymerisation process, which reduces manufacturing costs. To achieve this, stainless steel expanded mesh was coated in Pt, placed in the liquid monomer, and cured. However, the MEA £/kW calculations suggested that for methanol fuels, this particular method was not advantageous.

CONCLUSIONS

Cationic exchange (CE) and anionic exchange (AE) membranes have been developed using novel technologies based around hydrophilic polymers (Type 1) and radiation grafted co-polymers (Type 2). These were assessed for conductivity and fuel crossover before the most promising membranes were tested in a direct methanol fuel cell, and compared to Nafion 117, the current industry standard. A variety of fuel concentrations, oxidants and catalysts were tested at room temperature and low flow rates, with results quoted on a £/kW basis.

For CE materials, the Type 1 membranes and Type 2 membranes were calculated to cost £316/kW and £960/kW, respectively. These compare favourably with the cost of Nafion, at £1815/kW.

For AE materials, the Type 1 membranes and Type 2 membranes were calculated to cost £1019/kW and £5641/kW, respectively. Again, these are both cheaper than Nafion, at £6923/kW.

As, unlike Nafion the AE membranes developed in this project are true anion exchange materials, they offer the possibility of using cheaper catalysts. Therefore, fuel cells were tested where platinum (Pt) was replaced by palladium (Pd) on the fuel side of the cell. This was successful and resulted in a 36% reduction in the MEA £/kW. It is been predicted that a Pd-Ru cell would offer further MEA cost reductions and power density improvements.

Alternative oxidants were also briefly examined. It was found that replacing oxygen with hydrogen peroxide (H_2O_2) when using Pd as the catalyst produced a 66% reduction in MEA £/kW. Again it is predicted that a Pd-Ru catalyst with H_2O_2 will offer further cost reductions.

The objective of this project was to develop two alternative membrane technologies with significant cost/kW savings over Nafion 117. This objective has been achieved. Within ITM, the polymers developed during this project have been utilised on other research programs and now form an integral part of an expanding portfolio of materials. The AE Type 1 materials appear to offer potential in the electrolyser market, which ITM proposes to exploit. ITM have applied for five new patents that have resulted in whole or in part from this project (patent filing numbers, 0329459.2, 0417911.5, 0420961.5, 0504460.7 and one newly filed still awaiting an application number), at least two of these applications will undergo PCT application.

POTENTIAL FOR FUTURE DEVELOPMENT

ITM Power are confident that the technologies developed within this program have significant commercial potential. The combination of savings resulting from cheaper membrane and production costs, with the option of using alternative catalysts could allow ITM methanol fuel cells to penetrate the mass electronic device market.

The benefits of the technologies are not limited to methanol fuel cells. ITM have adapted the membranes developed within this project and used them within other research programs including the dual-liquid cell and flexible cell programs. It is believed that the electrolyser program will benefit most from this technology.

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