Laboratory plasmas applied to the hydrogen economy (fuel cells)

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Abstract

A major thrust of the hydrogen economy is to replace carbon-based fuels in transportation with hydrogen. One of the most promising candidates for this particular application is the PEMFC (Proton Exchange Membrane Fuel Cell) as it operates at low temperatures (less than 110 °C), is rather efficient, can be miniaturized and can cover a large power range. Fuel cell buses are being trialed in a number of countries as a result of the extensive research and development of these fuel cells for the past few decades.

Introduction

The properties of thin films deposited from a plasma are critically dependent on the flux, energy and charge state of the particles striking the growing surface [1]. Plasma sputter deposition of the platinum catalyst onto porous films of carbon has shown great promise: aggregates of platinum are detected in the film with a density profile which decreases away from the surface exposed to the plasma. The small size of the nano-aggregates allows very effective catalytic action necessary for efficient fuel cell operation [2,3,4]. The energy deposited by the plasma can also be used to functionalise commercial Nafion proton exchange membranes [5] suggesting the necessity of controlling the various plasma parameters for alternate scenarios such as the plasma deposition of PEM [6] and the continuous plasma deposition of the MEA (Membrane Electrode Assembly) [7]. Plasmas improve deposition quality, decrease process time, and open new paths for rapid commercialization. We are working to bring the 1970s plasma revolution in microelectronics to the hydrogen economy sector.

Laboratory Plasmas

Plasmas are ionised gases which can be used to etch, deposit or sputter materials. The interaction between the plasma and the surface to be treated can be chemical, physical or both. An important parameter in low pressure high density plasma processes is the ion bombardment. In inductively coupled plasmas operating at 13.56 MHz such as those presently used, ion bombardment can be controlled to develop various processes for the fabrication of PEM fuel cells components: a fuel cell consists of a PEM membrane (typically commercially available Nafion) sandwiched between two electrodes where each electrode consists of a conductive gas diffusion layer (carbon cloth or carbon paper) and an active layer containing the catalyst.

Plasma process of electrodes

Although a thick (about 30µm) active ink containing porous carbon, platinum, teflon and some nafion, is chemically made and “painted” onto the gas diffusion layer, the catalytic activity occurs mostly at the interface between the membrane and the electrode over a thickness of a few microns only. With plasma technology, it is possible to reduce the thickness of the catalytic layer (hence keeping the platinum use to a minimum), to increase the effective surface area for maximising catalytic activity for a fixed platinum loading, and to investigate the use of platinum gradients in the catalytic layer. Gradients can not be easily obtained when using chemical fabrication methods. An initial plasma process elaborated in our “CATAPULP” reactor [2,3,4] consists in an argon plasma sputtering a platinum target biased negatively so that the platinum atoms can subsequently be redeposited on the gas diffusion layer in the form of nano-aggregates to enhance the catalytic activity and minimize the amount of catalyst used.

It is of interest to set up a plasma process where both the carbon and the platinum can be deposited with predetermined profiles. This can be achieved in “CATAPULP” by adding a second carbon target in addition to the platinum target and by sputtering both targets with an argon plasma, where the sputtering rate control is obtained using various biases [7]. Another method consists in using carbon-containing plasmas such as methane or acetylene and this is investigated in our new “SOUTHERN CROSS” plasma reactor. The operating range of parameters is further increased by adding a temperature control of the electrode during the plasma process with the aim of further increasing the catalytic efficiency by depositing nano-aggregates of platinum on nano-structures of high conductivity graphitic carbon while maintaining a sufficient thin film porosity. The porosity has to be sufficiently high in order to prevent gas choking in high current fuel cell operation, as shown by simulations of low temperature fuel cell electro-chemical performances.

Plasma process of proton exchange membranes

Commercially available Nafion is an ion exchange membrane which is often used in PEMFCs. It consists of fluorocarbon chains terminated by sulfonic groups (SO_3^-), hence combining hydrophilic (in the bulk) and hydrophobic (at the surface) properties necessary for a good proton conductivity from the anode (H_2 side) to the cathode (O_2 side) and good drainage of the water formed from catalysis at the cathode. In operation the membrane needs to be hydrated.

Recent studies have shown how plasmas can be used for the surface treatment of Nafion [5] or for the plasma assisted deposition of ‘Nafion-like’ polymers [6]: Cho et al have shown that bombarding the surface of Nation with 1 keV Ar ion doses of 10^{15} to 10^{17}cm^{-2} changes the surface roughness and hydrophobicity of the membrane (with increased fuel cell performance) without altering the proton conductivity. We have studied the analysis of the change in hydrophobicity of Nafion samples treated in a low energy plasma diffusing from a radiofrequency helicon source in two distinct reactors “CHI KUNG” and “PIGLET”. Although our results are strikingly different to those obtained by Cho et al, we have shown that the treated surface exhibits a decrease in hydrophobicity with an increased energy dose. This has been modelled using low pressure plasma theory. The energy dose provided by the ion bombardment during the plasma treatment is responsible for this change while the energy dose from UV light has little effect for the present energy range of a few watts per square centimeter. Further experiments will focus on fuel cell performances using our new test bench.

Mahdjoub et al [6] have recently shown that thin films of plasma-polymerised proton conductive membranes could be deposited by plasma polymerization of trifluoromethane sulfonic acid (CF_3SO_3H), 1,3-butadiene and styrene mixtures in glow or afterglow argon discharges. Their results suggest that the type of discharge has an important impact on the micro-structure of the plasma deposited film and on the resulting proton conductivity. We are setting up a plasma system similar to that of Mahdjoub et al for the plasma deposition of proton exchange membranes.

Conclusion

Plasma technology applied to the fabrication of low temperature PEM fuel cells is being investigated. We have already shown that the platinum load can be reduced in plasma fuel cells for similar performances at low current and are developing a variety of plasma processes for the optimisation of the electrodes and membrane.

Acknowledgments

This research and development study is funded by an Australian Research Council discovery grant (DP0556821: Prof. R.W. Boswell, Dr C. Charles, and Dr A.L. Dicks) on "Development of new membrane-electrode assemblies for low temperature fuel cells".

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