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Increasing lifetime of polymer electrolyte membranes by incorporation of transition metal scavengers – A Review

Simon Auerbach

Fuel cells (FCs) are seen as an important component of a sustainable energy economy in the future. In polymer electrolyte membrane fuel cells (PEMFCs) the membrane plays a key role in providing a effective and long living power source. Various mechanisms lead to the degradation of PEMs, with the chemical degradation caused by radicals produced in the fuel cell having a major influence. Radcial scavenging has proven to be a good approach to significantly increase performance and lifetime. By incorporating transition metal oxides, a runtime extension from 200h to well over 1000h has been shown in accelerated stress test, as well as an improvement in cell performance as measured by polarization curves.

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Introduction

In a world where the effects of climate change and its consequences are increasingly being felt, and dependence on fossil fuels from countries such as Russia is leading to heated political discussions, hydrogen represents an important part of an independent, green energy economy.

In addition to production and storage, the efficient conversion of hydrogen to electricity using fuel cells is crucial. To make hydrogen cost-competitive, fuel cells must have a longer life than is currently the case to enable widespread applications in the automotive industry or in stationary power plants, for example.

PEMFCs represent a promising technology to meet these demands. One of the main reasons limiting their lifetime is the degradation of the PEM. Most PEMs available today are made out of perfluorosulfonic acid polymer (PFSA), which enables proton conductivity, acts as an electrical insulator and separates Hydrogen and Oxygen between the two electrodes of a FC1.

In addition to damage caused by mechanical stress, which is caused by different working conditions and humidity, for example, chemical decomposition is seen as a further important aspect. In use, the PEM is chemically attacked by radicals generated at the electrodes and thus increasingly loses its function, which ultimately leads to the failure of the FC2.

Limiting the degradation of such membranes is a key goal in developing cost-effective FCs. It has been shown that the incorporation of so-called scavengers, based on transition metal oxides, can significantly slow down the chemical degradation and thus significantly extend the lifetime of PEMFCs. These additives are able to quench the radicals by either donating or accepting electrons, preventing them from attacking the membrane, which otherwise would lead to degradation and the emission of fluoride which is of core importance in PEMs 3.

Three approaches, two based on the incorporation of cerium oxide (CeO2) and one based on the incorporation of cobalt, chromium and manganese oxides, respectively, will be discussed. In an accelerated stress test under open voltage conditions, all of them show a significant increase in lifetime, a decrease in fluoride emission and only a small, if even measurable, effect on performance.

Results

Lim et al. 4 prepared baseline membrane electrode assembly (MEA) by hot-pressing PFSA membranes with electrode gas diffusion layers (GDLs). To research the effect of incorporation of CeO2 on FCs the same GDEs were coated with a solution containing CeO2 powder.

Open cell voltage (OCV) accelerated stress test (AST), which is used to evaluated membrane degradation under harsh conditions, was used to determine the lifetime of the different MEAs. Figure 1 shows that while the baseline MEA failed after 186 hours the CeO2-MEAs lifetime extended to 1244 hours, which is six times as long. The same trend was observed for the fluoride emission rate (FER) and the corresponding thicknesses of the MEAs. Degradation of the membranes by radicals leads to fluoride being released from the polymer and therefore leads to loss of material. At the end of life, the baseline MEAs thickness was only 52% compared to the start, whereas the MEA with cerium only lost about 10% of its original thickness. At the end the FER was 40 times lower.

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