CO-tolerant Catalysts

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16.1 Introduction

Fuel cell systems offer the promise of economically delivering power with environmental and other benefits. Recently, polymer electrolyte membrane fuel cells (PEMFCs) have passed the demonstration phase and have partly reached the commercialization stage due to impressive research efforts. Nevertheless, there are still some technological challenges to be solved. Among those challenges, (i) choice of fuel (gasoline, methanol, or hydrogen), (ii) efficient fuel processing, with reduction of weight, volume, and carbon monoxide (CO) residuals, and (iii) development of anode electrocatalysts tolerant to CO at levels of 50 ppm (with a noble metal loading of 0.1 mg cm$^{-2}$ or less) are deemed to be the most significant barriers that PEMFCs must overcome to achieve complete commercialization. The first and second challenges are closely related to the source and purity of hydrogen as the fuel.

The simplest and highest performing PEMFC systems employ pure hydrogen as the fuel. Since H$_2$ storage and supply devices are an issue, feeding the anode with the reformate of liquid alcohols, gasoline, or natural gas is the most popular choice, as they are readily available. The alcohols, gasoline, or natural gas are reformed using steam, partial oxidation, or autothermal reforming to produce the reformate – a hydrogen-rich gas stream (H$_2$, 40–70%) containing carbon dioxide (CO$_2$, 15–25%), carbon monoxide (CO, 1–2%), and small quantities of inert gases, such as nitrogen and water vapor. However, at current PEMFC stack operating temperatures of around 80 °C, the membrane electrode assemblies (MEAs) within the stack cannot tolerate such high CO levels. Therefore, the reformate must be passed from the reformer to a shift reactor and then to a catalytic preferential oxidation (PROX) reactor to reduce the CO content to less than 100 ppm, and in some cases down to a few ppm. The reformate can then enter the stack and react in the anode electrocatalyst layer of the MEA. The additional reformer, shift and PROX reactors significantly complicate and add extra cost to the PEMFC system [1]. For instance, Cu-based catalysts [2] were ordinarily used as the shift-converter catalysts in plants; however, it is difficult to use a Cu-based catalyst in the domestic-use PEMFC system. The PEMFC system would be frequently turned on
and off, and when it was turned off, the Cu catalyst would be easily oxidized by steam and air, and eventually deactivated. Therefore, precious metal catalysts such as Pt catalysts supported on CeO$_2$-containing oxides were used in the PEMFC system. On the other hand, Pd [3], Au [3], Pt, or Ru [5] is used as the catalyst for preferential oxidation of CO at low temperature. Among these, the Ru catalyst exhibited high performance for preferential oxidation of CO and long-term stability under a low O$_2$/CO molar ratio [5]. In any case, considerable amounts of precious metals were used in both a shift converter unit and a CO preferential oxidation unit, resulting in high cost. Moreover, this complicated system containing a CO-removal unit led to low efficiency and reliability. Therefore, developing CO-tolerant anode catalysts is a key priority. The US DOE 2011 targets for fuel cell stack CO tolerance are 500 ppm on steady state (with 2% max air bleed) and 1000 ppm on transient [6].

In a PEMFC, when operating with pure hydrogen at practical current densities, the anode potential is typically less than +0.1 V (vs. RHE (reversible hydrogen electrode)). Under such operating conditions the cell potential is only slightly lower than the cathode potential and the MEA performance essentially reflects the cathode operation. However, when using reformate as a fuel, the CO in the reformate stream binds very strongly to the Pt electrocatalyst sites in the anode catalyst layer, at the typical MEA operating temperature of 80 °C. Even at ppm levels of CO, the CO coverage is above 0.98 [7]. The adsorbed CO prevents the dissociative electrosorption of hydrogen and dramatically lowers the cell potential produced by the MEA, since a much higher anode potential is required to sustain the rate of hydrogen electrooxidation [8]. Poisoning of Pt anode electrocatalysts by CO is deemed to be one of the most significant barriers to be overcome in the development of PEMFC systems.

In addition, CO was found to be a poisoning adsorbate during the oxidation of methanol and other small organic molecules [9]. An important although not unique aspect of the catalysis of methanol oxidation in direct methanol fuel cells (DMFC) is related to the catalysis of CO oxidation. Therefore, methanol and CO oxidation reactions are both discussed in several reviews [10–12].

There are a number of ways to overcome the CO poisoning of electrocatalysts [13–15], namely: (i) advanced reformer design; (ii) use of CO-tolerant catalysts; (iii) oxidant bleeding into the fuel feed stream; (iv) employment of a bilayer (composite) anode structure; (v) higher cell operating temperature; (vi) use of membranes for CO separation; and (vii) pulsing the cell voltage to low values during cell operation, forcing the anode potential to operate for a short time at a potential positive enough to electrochemically oxidize CO to CO$_2$.

(i) Advanced reformer design. Most of the reformers, including the auxiliary processors that are currently available, are capable of producing a CO content of 50 ppm or less after a warm-up period of up to 2 h. To acquire the bleeding oxidant effect by modifying the reformer, many researchers have considered the possibility of designing a new reformer to which auxiliary processors are fitted for clean-up steps, e.g., as shift converters and a selective oxidizer [16–18]. These methods would, however, increase the complexity and cost of the fuel cell system. Even when these additional stages are used, it is difficult to maintain low CO levels