

Sol-Gel Based Silica Electrodes for Inorganic Membrane DMFCs

by Hyea Kim

Direct methanol fuel cells (DMFCs) have attractive cost and energy-density features especially for portable, low-power electronic devices (μW to mW), such as wireless sensors. Low methanol cross-over is critical to achieving high energy efficiency and long life since fuel loss through the membrane is the dominant loss mechanism in long lifetime devices. Previously, the polymer membrane was replaced with an inorganic glass membrane resulting in a significant decrease in methanol permeability.¹ However, the DMFC performance was unstable because the polymer-based ionomer used in the catalyst ink was incompatible with the glass membrane. The coefficient of thermal expansion mismatch between the electrode and membrane contributed to high contact resistance. There are long-term reliability issues with the water-rich, polymer ionomer soaking in the aqueous methanol of a passive DMFC.

In this project, electrodes based on glass-based ionomers were investigated. Platinum-ruthenium glass electrodes (PtRu/C-SiO_2) were prepared by incorporating the PtRu/C nanoparticles into a silica-based matrix. The SiO_2 matrix was

synthesized through the sol-gel reaction of 3-(trihydroxysilyl)-1-propanesulfonic acid (3TPS) and 3-glycidoxypropyl trimethoxysilane (GPTMS). The structures of 3TPS and GPTMS are shown in Fig. 1. The sulfonic acid group in 3TPS provides proton conductivity in the catalyst layer. The three hydroxyl groups of the 3TPS react with water and condense to form a silica matrix encapsulating the catalyst in the matrix. The epoxy content of the GPTMS improved the mechanical properties of the electrode by crosslinking with the silicon dioxide matrix.

The size and distribution of the PtRu/C particles was controlled by changing the microstructure and properties of the gel matrix. The effect of gelation time, mole fraction of reactants within the sol, curing temperature, and glass ionomer content were investigated. The adhesion of the catalyst layer on the membrane, electrochemical activity for methanol oxidation, and decrease methanol cross-over through the membrane were investigated. The optimum glass electrode was composed of 90 mol% 3TPS and 10 mol% GPTMS and the catalyst-to-glass ratio was 1:5. The 3TPS and GPTMS were allowed to react for 3 h before coating and the membrane followed by curing at 80°C .

The sheet resistance of the electrode was decreased by electrolessly plating PtRu on the PtRu/C catalyst.^{2,3}

The sheet resistance decreased and the electrochemical activity of the electrode increased after the electroless PtRu deposition. The methanol permeability decreased by 65% with electroless deposition because the membrane area exposed to the methanol decreased, as shown in Fig. 2a. The decrease in methanol permeability is a benefit, if the electrochemical activity of the electrode can be maintained. The catalyst activity increased with PtRu deposition, as shown in Fig. 2b, which was likely due to a higher PtRu area.

Finally, a glass MEA was fabricated using the sulfonic acid-functionalized glass membrane.¹ The fuel cell life test was performed at a constant voltage of 400 mV. As shown in Fig. 2c, the current density increased from 200 to $340 \mu\text{A cm}^{-2}$ over the first 160 h, and remained constant thereafter.

Acknowledgments

The author gratefully acknowledges ECS for the Colin Garfield Fink Summer Fellowship and Prof. Paul A. Kohl for his guidance and encouragement. ■

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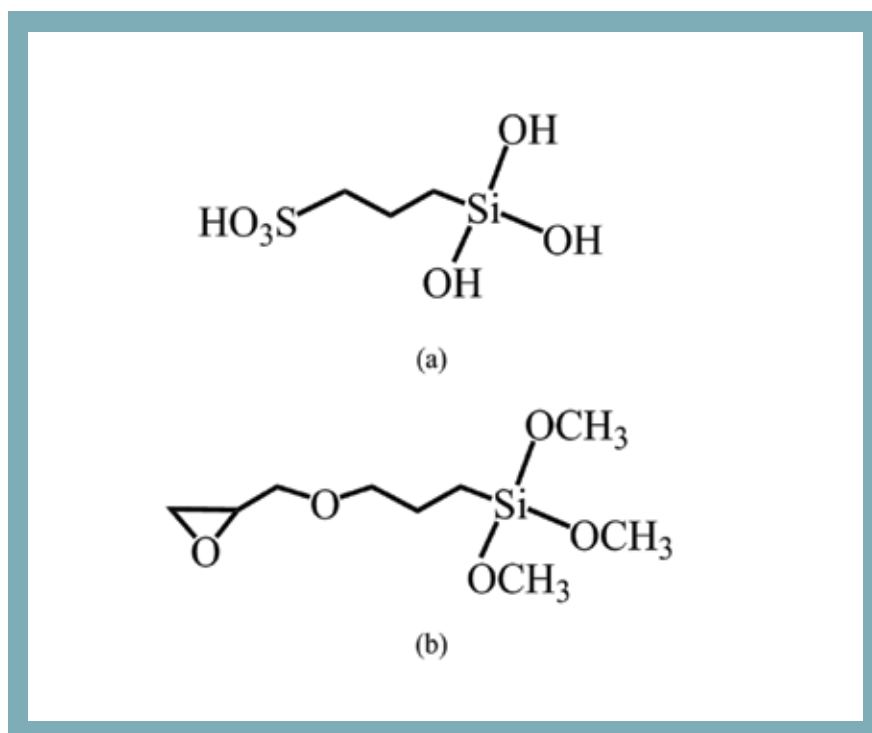
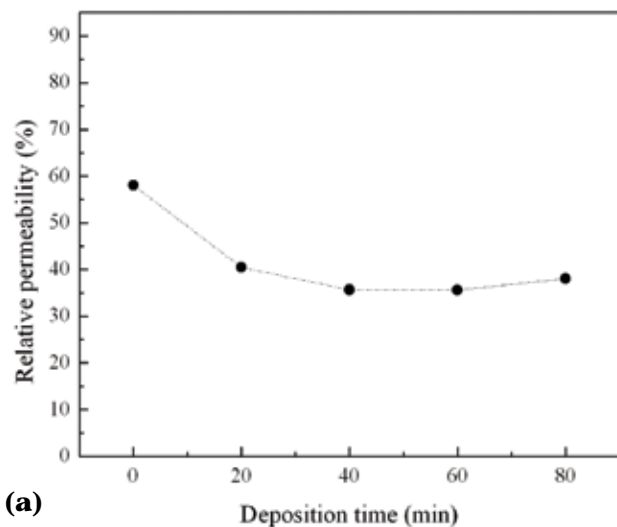
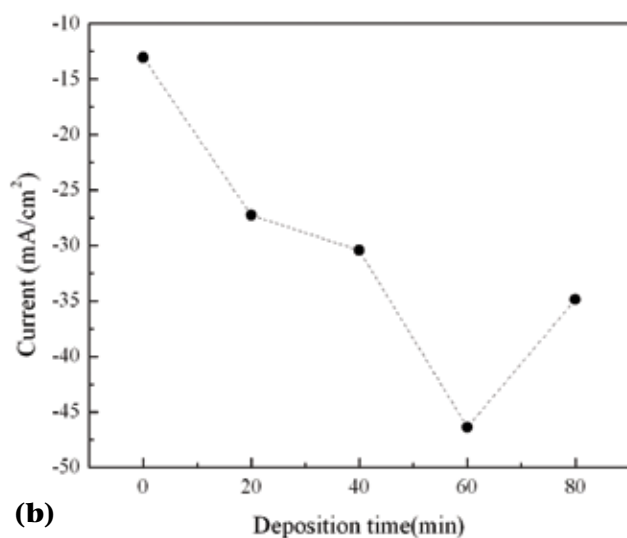


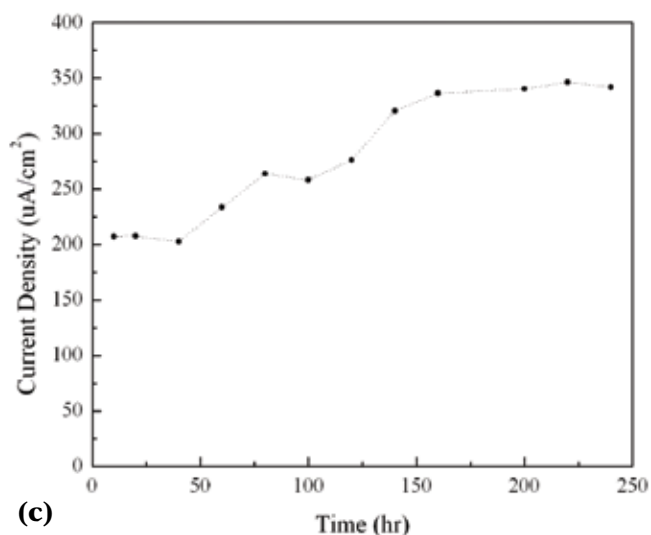
FIG. 1. The chemical structure of (a) 3TPS, and (b) GPTMS.



(a)



(b)



(c)

Fig. 2. (a) Relative methanol permeability as a function of the PtRu electroless deposition time with a 1:5 catalyst-to-glass ratio, optimized electrode; (b) current density at 0.2V (vs SCE) as a function of the PtRu electroless deposition time with a 1:5 catalyst-to-glass ratio, optimized electrode; (c) life time test for a fully passive DMFC with a glass membrane and glass electrodes at 0.4 V; 23°C, 0.5 M methanol.

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