

Comparison of Catalyst Performance for a Direct Methanol Fuel Cell Fabricated in Low Temperature Cofired Ceramics (LTCC)

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Abstract

Integrating a power source, such as a direct methanol fuel cell (DMFC) into a low temperature cofired ceramic (LTCC) based microsystem allows for the next level of microsystem integration. In our LTCC-based DMFC structure, a porous silver tape is used to replace the traditional carbon electrode. Catalysts play a critical role in fuel cell performance. Two catalyst-preparing methods were evaluated, one cofired and one post fired, using platinum and ruthenium resins for the catalysis source. The cofired anode microstructure demonstrated many whiskers with higher degree Pt-Ru alloy and Ag while the post fired anode exhibited Ag, lower degree Pt/Ru alloying and RuO₂. Cyclic voltammetry results show that the cofired catalyst has a better catalyst effect than that of post fired catalyst and both had a better catalysis performance than the catalyst on a standard carbon based anode. These specific catalyst microstructures contributed to the better catalysis effect in the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR) respectively.

Key Words: LTCC, DMFC, catalyst,

1. Introduction

Miniature batteries or fuel cells, such as the direct methanol fuel cell (DMFC), are key future technologies in electronic micro-systems miniaturization [1]. Micro electromechanical system (MEMS) technique have been used for manufacturing miniature DMFCs, but MEMS processing requires complex and precise processing such as chemical vapor deposition, etching, photolithographic process, catalyst electrodeposition etc. on wafers [2]. DMFCs have been fabricated using low-temperature co-fired ceramic (LTCC) as a hermetic structure, providing channels and cavities, while the electrode structure used was a standard carbon based electrode used in standard DMFC construction [3]. This “hybrid” structure required mechanical assembly, minimizing its application as a miniature device. In this effort, a DMFC was fabricated using LTCC, which allows a layered construction with embedded micro-channels and integration of numerous components. LTCC allows a wide range of enhanced electronic functions, such as high density interconnects, enhanced thermal management and high frequency performance to be built into the ceramic micro system [4]. The DMFC is fabricated within the structure of a cofired LTCC, using a porous Ag tape as an electrode structure, post-fired and cofired LTCC processing.

fugitive graphite inserts to develop cavities to hold either the methanol or the Nafion proton exchange membrane (PEM) and channels and open vias that can complete the fluidic structure. Integration of a catalyst within the anode and cathode structures of the cell is an important aspect when considering device structure and processing since the catalyst directly affects the fuel cell performance. In the standard carbon based electrode system found in DMFC, numerous techniques for catalyst preparation have been developed, including impregnation [5], colloidal [6], micro emulsion [7], and co-precipitation [8]. These chemical methods generally use toxic, combustible or explosive reactants, which are filtered, washed, centrifuged, dried under vacuum and then reduced under hydrogen, making large-scale production hard to control and costly. Considering the LTCC process, the catalyst is prepared by simple pyrolysis, greatly decrease the factors affecting the catalyst performance. Typically, catalyst performance is enhanced by catalyst with smaller physical size and narrow distribution of particle size. Cofired catalyst on silver can form the high degree alloyed catalyst. The molecular orbital theory calculation predicts that the second transition element such as Zr, Mo, Pd, and Ag has a high activity for OH bond reduction comparable to that of Ru [11]. This work evaluates the catalytic reaction comparison between

Experimental

The anode and cathode material starts with a porous Ag tape. The porous silver tape is made by mixing silver powder and graphite powder in a ratio to yield the desired porosity, blending with a standard tape cast formulation (dispersant, binder, plasticizer and solvent) and doctor blading the slurry to the desired thickness. The morphology of the porous Ag tape is shown in Figure 1. Platinum resinate and ruthenium resinate are the catalyst source. This work evaluated the difference in performance between a cofired and a post-fired catalyst structure.

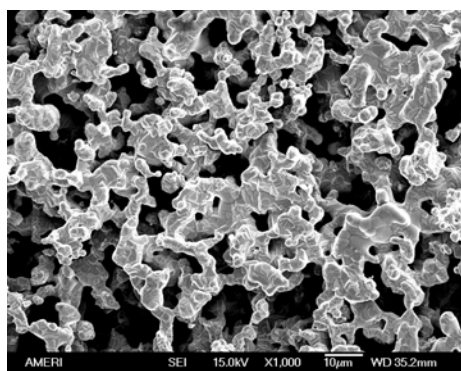


Figure 1. The SEM photomicrograph of porous Ag tape

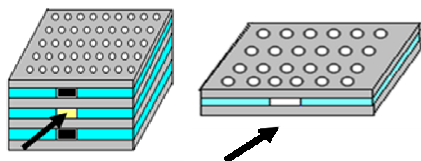


Figure 2 Cell structure formed by post-firing (left) and cofire (Right)

To evaluate the performance of the catalyst in the fuel cell, test cell consisting of an anode and cathode structure separated by a PEM layer were developed. Closed cavities or channels for the methanol were not required. The porous Ag tape was used as the electrode layers and thin cavities were fabricated using fugitive carbon tape (Thick Film Technology, Everett, WA 98024) inserted into laser machined Dupont 951 LTCC tape and then laminated together at standard times and pressure for 951 tape. The stacks were fired to the follow process: ramp at 5°C to 450 °C, hold for 2 hrs to remove the tape organic phase, then ramp to 650 °C and hold for 3 hrs to remove the carbon tape and fire to 850 °C for 15 min.

Fig. 2 demonstrates the cell structure of cofired and post fired processing. For the cofired catalyst, the catalyst is added to the Ag in the porous

tape formulation. In the catalyst preparation, 64 mg catalyst is added into 3g Ag powder prior to graphite addition and tape casting. In the post fired case, a thin cavity was fired between tow layers of porous silver tape for each electrode, the catalyst resinate mixture was added and then resinate fired. In each case, the molar ratio of Pt-Ru is 1:1 for the anode and pure Pt for the cathode. The post- fired processing was done at 500 °C, as determined by thermogravimetric analysis of the decomposition of the resinate material.

A solution of liquid Nafion and PTFE (20 ~30 wt%) is injected into the cavity separating the electrodes and heated to 120 °C for 15 min to form the PEM membrane. Obviously, the cofired process exhibited the simplest structure and processing.

The catalyst characterization is done by X-ray diffraction (Siemens D500), scanning electron microscopy (JEOL JSM-6330F) and transmission electron microscope (TEM, Philips CM 200). The electrochemical measurement of cyclic voltammetry (CV) was performed with a Solartron 1287/1260 computer controlled impedance system and a conventional three-compartment electrochemical cell. A Pt sheet was used as the counter electrode. The saturated calomel electrode (SCE) was used as a reference electrode. All the potentials were quoted with respect to the reference SCE electrode. Methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) experiments were conducted in 0.5 M H₂SO₄ solution in 1.0 M CH₃OH and 0.5 M H₂SO₄ solution respectively.

Results and discussion

1) Anode catalyst physical characterization

The XRD pattern shows the main phases of the post-fired anode catalyst are Ag, Pt-Ru alloy and RuO₂, as shown if figure 3. Particle size calculated from line broadening from the Scherer equation indicated a particle size of 5.6 nm, consistent with the TEM analysis (4.8 nm). The Ru atomic fraction in the alloy is about 0.17 from non-dispersive X-ray spectroscopy, implying that only a small part of Ru was alloyed with the Pt while the remained was present as RuO₂

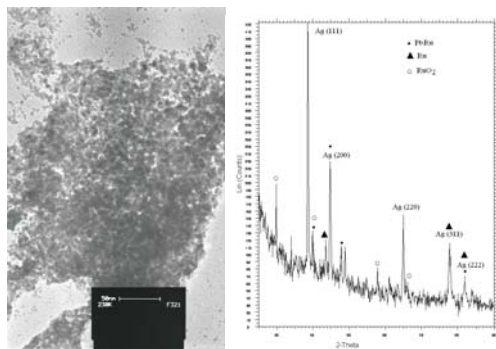


Figure 3 .TEM of catalyst and XRD pattern of post-fired catalyst

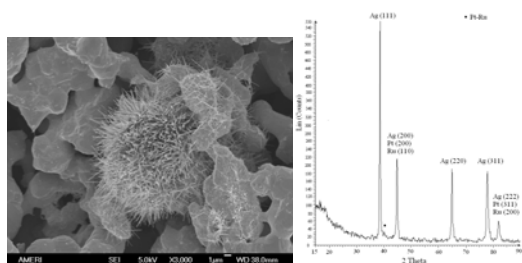


Figure 4 SEM of catalyst and XRD pattern of cofired catalyst

For the cofired anode catalyst, a Pt-Ru alloy and small amounts of precipitated Ru are demonstrated. The microstructure of the cofired catalyst exhibits a large amount of whiskers on the solid phase surfaces in the pore structure. EDX analyst in Figure 4 shows the main phase of whiskers is Ag with a small amount Ru. The whisker diameter is about 50 nm and the length is about 1.2 μm .

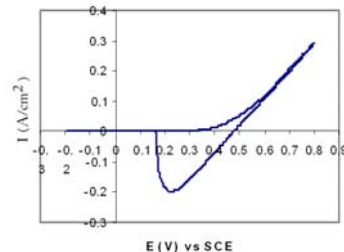
2 Cathode catalyst physical characterization

The cathode was processed only using Pt resinate. The catalyst demonstrated separated nano particles of Pt on the Ag porous matrix.

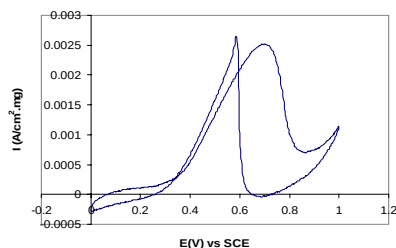
3) Electrochemistry characterization

The onsite potential of the reaction will affect the performance of the catalyst effect for the cathode and anode..

The onsite potential of porous Ag is about 0.47V (vs SCE) (Figure 5a) and the methanol oxidation reaction (MOR) with the Pt-Ru catalyst range is from 0.34 to 0.7 V (vs. SCE) (Figure 5,b) when measured on a carbon electrode. Carbon is used as it has no catalytic effect on the methanol oxidation so figure 5b represents the response of only the catalysis.



(a)



(b)

Figure 5. Cyclic voltammetry of porous Ag tape (a) and Pt-Ru catalyst in 0.5M H_2SO_4 at 60 °C with a sweeping rate 20 mV/s (b).

For the porous Ag anode, the voltage above 0.47V in Fig. 6(b) is the mixed contribution from Ag and methanol oxidation from the Pt-Ru catalyst since the onsite reaction of Ag is 0.47V (vs. SCE). It is hard to distinguish the contribution from the catalyst on the MOR above 0.47 V (vs. SCE), however the voltage before 0.47V (vs. SCE) is defiantly from catalyst.

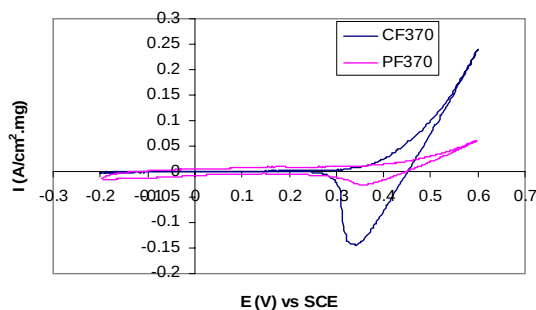


Figure 6. The cyclic voltammetry of post-fired (PF) and cofired (CF) catalyst for the anode at 60 °C with sweeping rate 20 mV/s 0.5 M H_2SO_4 solution in 1.0 M CH_3OH

The methanol oxidation reaction (MOR), as shown in figure 6 as measured by cyclic voltammetry at the Ag anode demonstrates that the cofired anode (CF) acts as a better catalyst than the post-fired (PF) electrode.

From the Figure 5 and 6, it is obvious that both cofired and post-fired catalysts have a better catalyst effect than the same catalyst on carbon.

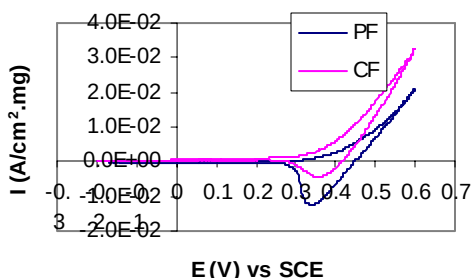


Figure 7. Cyclic voltammetry of post-fired and cofired catalyst for the cathode in 0.5M H₂SO₄ at 60 °C with sweeping rate 20 mV/s.

Figure 7 is the cyclic voltammetry analysis of the cathode catalyst. Similarly, we can see the cofired cathode provides a higher catalyst effect than that of post-fired catalyst (from the section of the curve before 0.47V (vs. SCE)). The generally accepted explanations of the cathode catalyst effect are from electronic factors, i.e. the change of the d-band vacancy in Pt upon alloying and/or by geometric effects (Pt-coordination number and Pt-Pt distance) [12], and the decrease of the Pt oxidation state [13].

4. Conclusion

1. In the cofired anode microstructure, the catalyst exhibits whiskers of a Pt-Ru alloyed microstructure. The post-fired anode catalyst represents a lower degreed Pt-Ru alloying and RuO₂ with a particle size of 4.8 nm.
2. Both post-fired and cofired catalysts on Ag demonstrated a better catalyst performance than the catalyst on carbon electrode.
3. The electrochemistry measurement for the both anode and cathode catalysts structures indicated a higher catalysis effect in the cofired processing than that of post-fired processing. The enhancement of the anode catalyst effect could come from the higher surface area of the whiskers or the uniform composition.

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