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Studies on Methanol Fuel Cells*

by

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Methanol 燃料電池에 關한 硏究

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要 約

Methanol 燃料電池는 安價인 液體燃料의 使用, 低溫에서의 可動, 特히 電氣化學的 反應性 等에서 볼 때, 可搬型 動力電源으로 有望한 燃料電池系라고 본다. 本 論文은 再現性이 크고, 低過電壓인 同時에 높은 電流密度에서 動作할 수 있는 多孔性인 活性化 電極의 製作 및 燃料電極의 分極特性을 檢討하였다.

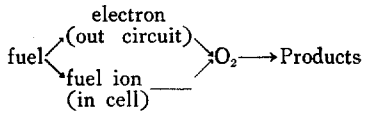
INTRODUCTION

Work on fuel cells for industrial, motive, and portable power units has been conducted on an increasing scale during the past decade. Although fuel cells are finding important uses in military and space applications[1], significant commercial applications are likely to be in use within ten years.

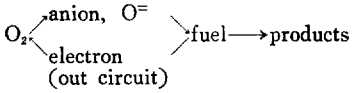
Many progress reports achieved with fuel cells, such as hydrogen-oxygen types, H_2—O_2 ion-exchange membrane, redox systems, hydrazine, methanol, molten martrix fuel cells and others are represented both at the technical society meetings and publications.[13] For example, in 1968, 138 papers and 121 patents (U. S. A., 72; Fr., 29; Brit., 7; Ger., 9; others, 4) appeared in Chemical Abstracts.

In principle, an electrochemical reaction could take place in a fuel cell:

Anodic reaction,



Cathodic reaction,



Methanol is an attractive fuel for fuel cells because of its electrochemical reactivity, availability, low cost and low-temperature operation. Several studies have been reported on the anodic character of nickel[2], doubly activated nickel plate[3], palladium[4], platinum-rhenium catalysts[5] and on the mechanism of the anodic oxidation[6] at platinum electrode for methanol fuel cells. Müller[7] published various theories to explain the anodic oxidation of formaldehyde, being principally concerned with the mechanism of the formation of hydrogen. In view of the energy utilization, complete oxidation to carbonate ions is desirable by use of platinum or palladium black nickel fuel electrodes because platinum

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and palladium has a particular affinity for hydrogen.

In this paper, quantitative studies on the anodic polarization characteristics of fuel electrode are investigated. A reproducible technique for depositing a highly active platinum or palladium black onto nickelnized nickel electrodes was developed. This activation procedure has resulted in the development of solid porous anodes having high limiting current density and particurarly low polarization for methanol fuel cells.

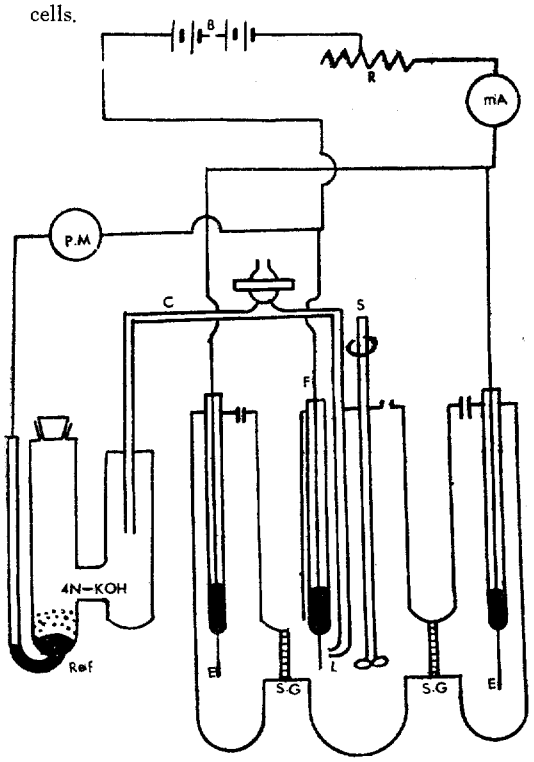

Fig. 1. Half-cell assembly for polarization measurements

B. Battries
C. Luggin Capillary Bridge
D. 4N-Methanol/l, 4N-KOH
E. Counter Electrode
F. Fuel Electrode
S. Stirrer
S. G. Sintered Glass
Ref. Hg/HgO, 4N-KOH reference electrode
L. Luggin Capallary
P. M. Potentiometer
mA. Milliammeter
R. Rheostat

EXPERIMENTAL

Apparatus. The three-compartment type cell is provided with an electrolyte bridge which is drawn out in to a Luggin capillary, a stirrer, two counter electrodes, a test fuel electrode, and a porous sintered glass disc to separate the anode and cathode compartments. The Luggin capillary bridge is connected to an H-type's 4N-KOH, mercury-mercury oxide reference electrpde and whole apparatus is placed in a thermostated bath at 50°C. When elctrodes are studied in an half-cell, current from an external source is supplied to the circuit as shown in Figure 1.

A Yokogawa potentiometer Model D-1B was used to obtain voltage reading. The conductance was measured with a Yanagimoto conductance bridge Model MY-7.

Materials. Reagent grade chemicals were used without further purification. A bright nickel plate and a 100 mesh screen nickel plate with surface area of 24 cm^2 (thickness, 0.5mm; length, 40mm; width, 30mm) were used as the electrode species[9].

RESULTS AND DISCUSSION

Preliminary Examination

Reference electrode[8]. As the reference electrode in the basic solution, mercury-mercury oxide with 4N-KOH reference electrode was used for the measurement of potentials. It was observed that, analagous to its behavior in calomel electrode, mercury oxide is very slightly soluble in water. The reference electrode was prepared by contacting two-phase mercury saturated with mercury oxide, 4N-KOH solution.

The potential of the reference electrode is determined by the hydroxide ion activity. The half-cell potential of 4.047N-KOH and 0.801N-KOH reference electrodes were measured to be -0.1771 volts and -0.1271 volts versus saturated calomel reference electrode with standard deviation 1.7 mV. and 2.2 mV., respectively.

The potential differences measured between the saturated calomel reference electrode and the electrodes containing various concentrations of potassium hydro-

xide agreed well with the calculated potentials for the mercury oxide reference electrodes as shown in Figure 2.

Effect of temperature. The polarization characteristics of the fuel electrodes for the anodic oxidation of methnol were measured at the temperature of 20, 30, 40, and 50°C. The fuel cell electrode potentials, in general, shifted to the more negative potential by elevating the temperature. However, during the experiments the temperature of the electrolyte was maintained at 50°C because the vaporization of methanol becomes violent.

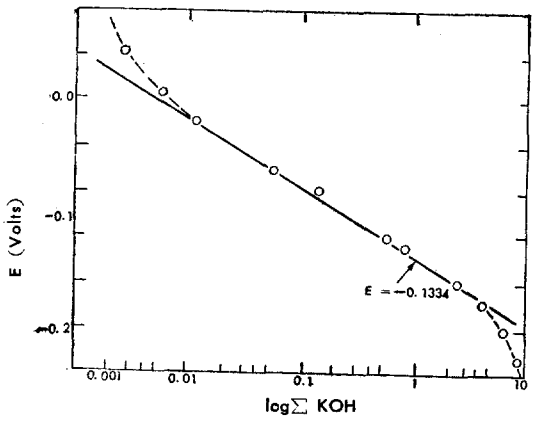

Fig. 2. Half-Cell Potential-Concentration Curve
Points are experimental, and solid line is theoretical.

Effects of concentration of KOH and methanol. Potassium hydroxide of various concentrations were used as an electrolyte solution, and the effect of rate of performance of electrolytes was examined. It was obvious that the polarization potential of fuel electrode changed to the more negative potential by increasing the concentration of potassium hydroxide. For example, at 0.5 and 3mA/cm² current density, the potential differences measured between 2N-KOH and 5N-KOH were to be 30 and 20 millivolts, respectively. On the other hand, It was observed that the doubly activated electrodes, give a higher limiting current value and better characteristics with an increasing methanol content.

Current-Voltage Curves

The polarization characteristics of the bright nickel plate, nickelnized nickel plate and nickel black plated 100 mesh screen electrodes are given in Figure 3, which shows that these electrodes are not only inactive, but have an exceedingly low limiting current density.

As shown in Figure 3, the current value at which the potential suddenly rises is observed with increased current density. The fuel electrode could not keep the negative potential for a long time at the polarization measurements. Consequently, this electrode seems to be unfavorable for methanol fuel cells.

In inducing the best condition for preparation of the fuel electrode the plating conditions of nickel black, doubly activated nickel black with platinum and palladium black electrodes were made by the electro plating in an acidic Watt's bath with 100 mesh screen nickel plate. Breiter's work[9] showed that platinum[10] and palladium[4] are virtually active catalysts for the anodic oxidation of methanol. Also, it has been reported that the platinum and palladium electrodes showed more negative potentials and higher limiting current density.

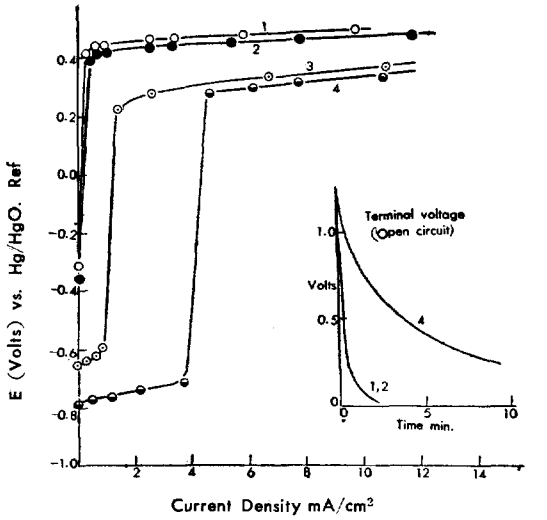

Fig. 3. Polarization characteristics of nickel fuel electrodes and terminal voltage change

Curve 1. Bright plate nickel
〃 2. 100 mesh screen nickel
〃 3. Nickel-black plated: 4.8 A/dm² in nitric acid normal Watt's 2ath, 20min.
〃 4. Nickel-black plated 100 mesh screen Nickel: 7.44 A/dm², 30min., nitric acid normal Watt's bath.

The polarization characteristics of these electrodes are shown in Figure 4. It was observed that the potentials at high current density changed to the negative upon increasing current.

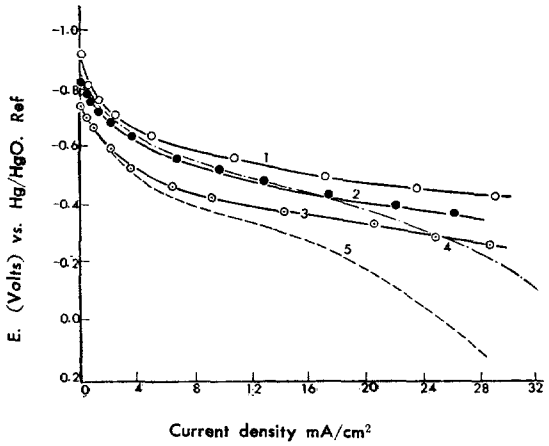

Fig. 4. Activated fuel electrode potentials as a function of current density

Curve 1. Pt and Pd black plated 100 mesh screen Nickel.
〃 4. Same electrode after 30 hours.
〃 2. Pt black plated Ni plate electrode.
〃 3. Activated by immersion plating with Pt-containg solution.
〃 5. Same electrode after 24 hours.

Although the limitations of the methanol electrode due to mass-transfer processes cannot be precisely defined, the process taking place at the surface of the electrode will be governed by the laws of ordinary chemical kinetics, if the concentration polarization is absent.

As shown in Figure 5, a nearly linear relationship between the polarization and the logarithm of current density can be obtained. Tafel's equation[11] represents, $\eta = a + b \log i$, where a and b are characteristics for electrode process and η is over-potential at the applied current density. From this linear Tafel plots for methanol the slope b was calculated as 0.212. This value is good agreement with Buck and Griffith's[12] who found a value for b at 25°C of 0.21-0.28 which was independent of pH for values from 10 to 14.

Surface Covering and Life-Span

The surface covering of the activated fuel electrodes was examined as a function of time, potential, and anodic constant-current conditions being used as shown in Figure 6 and 7. When the external polarization circuit was open, the potential of the electrode graduately reached the open circuit value. It was observed that the potential of nickel black deposited electrode recovered more slowly than that of the platinized and palladized black electrodes.

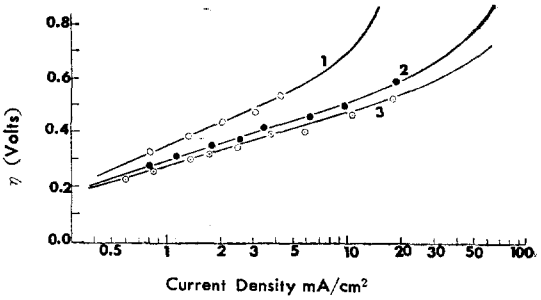

Fig. 5. Plots of polarization potential versus log. current density (Tafel plots)

Curve 1. Activated by immersion plating with Pt-containing solution.
〃 2. Pt Black plated Ni plate.
〃 3. Pt black plated 100 mesh screen nickel.

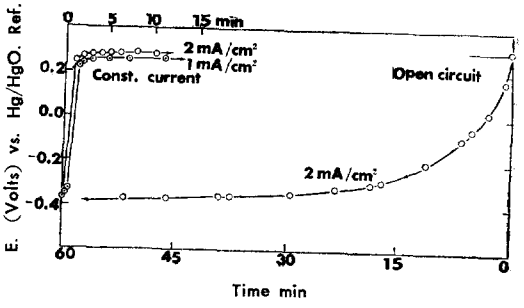

Fig. 6. Potential-Time curves of the nickel black plated electrode

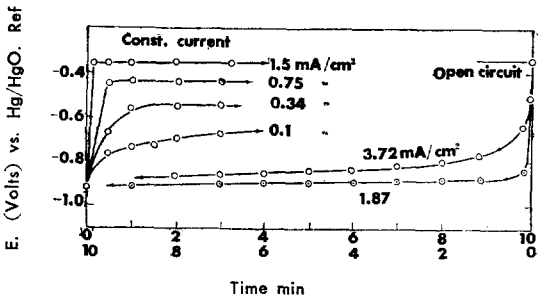

Fig. 7. Potential-time curves of platinum black plated with nickelnized 100 mesh screen nickel

In the life tests of the activated fuel electrodes, the potentials shifted to more positive potential in 30 hours as shown in Figure 4 in curves 4 and 5. It seems that the activated nickel and platinum black were deterirated by the charging current and the increasing current density.

ACKNOWLEDGMENT

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