Electrochemical Promotion of Pt Catalyst for The Oxidation of Carbon Monoxide

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Abstract

Electrochemical promotion of the reaction rate was investigated for CO oxidation in a solid electrolyte catalytic reactor where a thin film of Pt was deposited on the yttria stabilized zirconia as an electrode as well as a catalyst. It was shown under open circuit condition that potential was a mixed potential of O_2 exchange reaction and electrochemical reaction induced by CO. The effect of electrochemical modification on the CO oxidation rate was studied at various overpotentials and P_{CO}/P_{O2}.

1. Introduction

Development of solid electrolytes connects heterogeneous catalytic reactions and electrochemistry. This type is called a solid electrolyte electrochemical cell, and there are three applications.

First, it can be used as solid oxide fuel cell type reactors, or chemical cogenerator where electric power and useful chemicals are simultaneously produced. Electrochemists have called it electrogenerative process. NO [1], HCN [2], SO_2 [3,4], $C_6H_5CH=CH_2$ [5] have been produced with electricity using this type of reactor.

Secondly, it can be applied to a typical electrochemical reactor where electrochemical reactions are driven by the voltage or the current supplied to the catalytic electrode of solid electrolyte electrochemical cells. The change in the reaction rate Δr is only limited by the following Faraday's law

$$\Delta r = \frac{I}{2F} \quad (1)$$

where I is the current and F is the Faradaic constant. This kind of electrochemical reaction includes electrochemical electrolysis of H_2O [1], decomposition of NO [6], hydrogenation of CO [7], and conversion of CH_4 to C_2 hydrocarbons [8].

The third application is electrochemical catalytic promotion, which is often called nonfaradaic electrochemical modification of catalytic activity (NEMCA) effect [9]. When current or voltage is applied to the working electrode and the metal-solid

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electrolyte interface is sufficiently polarized as well, then the catalyst potential is altered as ions are supplied or removed to or from the surface of metal catalyst across the electrolyte by migration. The observed change in the reaction rate becomes dramatically larger than expected by the supplied current to the catalyst surface as follows,

$$\Delta r \gg \frac{I}{2F} \tag{2}$$

This is because each ion supplied onto the catalyst surface can cause many chemisorbed molecules to react.

The degree of the catalytic activity promotion by the NEMCA effect can be defined as the enhancement factor Λ and the rate enhancement ratio ρ [10].

$$\Lambda = \frac{\Delta r(catalytic)}{I/2F} \tag{3}$$

$$\rho = \frac{r(catalytic)}{r_0(catalytic)} \tag{4}$$

where r_0 is the catalytic reaction rate under the open circuit condition. The NEMCA effect appears when $|\Lambda|>1$.

Electrochemical catalytic promotion requires electric power, but the cost of this energy is negligible compared with the value of the chemicals produced. In addition, since only a small amount of current is required to induce the NEMCA effect, the catalytic reaction can be carried out at low temperatures. Recent demonstration of NEMCA using mixed ionic-electronic conductors [11], Nafion [12] or aqueous alkaline solutions is also noteworthy.

In this study, the effect of NEMCA on the rate of CO oxidation was examined in terms of the overpotential at the various P_{CO}/P_{O2} ratios. Oxygen exchange reaction and the normal CO oxidation under open circuit conditions were also investigated before the circuit was closed and the overpotentials were applied.

2. Experimental

2.1. Preparation of the Reactor

In order to induce the NEMCA effect, the following type of solid electrolyte reactor is usually used.

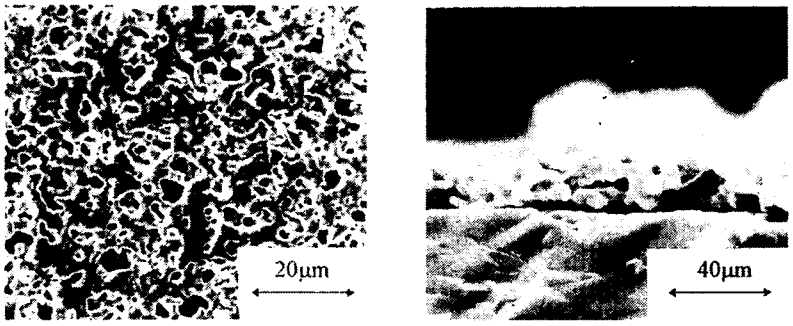
reactant, metal catalyst | ZrO_2 (8mol% Y_2O_3) | M, O_2 (5)

where the metal catalyst is the working electrode and M is the counter electrode.

To prepare the solid electrolyte, 8mol% yttria stabilized zirconia (YSZ) powders (Tosoh, TZ-8Y) were isostatically pressed under 100 Mega Pa to form a disk. This disk was then sintered at 1450℃, resulting in the final YSZ disk with the diameter of 24mm and the thickness of 1.5mm. The bulk density was almost 98%

of the theoretical density [13].

Pt was chosen as a material to act as an electrode as well as a catalyst. To deposit a thin film of Pt catalyst on the YSZ disk, the screen printing method was used where platinum paste (Johnson-Matthey, TR-7905) was printed on the YSZ disk. The deposited Pt paste was calcined in air at 900℃ to remove the binder and the impurities in the paste. The SEM image as shown in Fig. 1 revealed that the deposited Pt electrodes on the YSZ disk was a porous thin film, and it consisted of a crosslinked network of sintered Pt powders.



(a) Top view (b) Side view

Fig. 1. SEM image of the Pt electrode on the YSZ disk.

The electrode/YSZ disk was attached to one end of the alumina tube using the sealants. Therefore, we assumed that the characteristics of the reactor was similar to the constant flow stirred tank reactor. The flow rate of the reactants was controlled by mass flow controller. The reactants were pure (99.99%) carbon monoxide and oxygen(99.99%) diluted with pure (99.99%) helium.

2.2. Experimental Procedure

(1) Oxygen Exchange Reaction

When the temperature of the reactor approached to 500℃, helium was introduced at a flow rate of 400sccm. If the open circuit potential showed a stable value under the helium atmosphere, P_{O2} in the reactor was changed by controlling the flow rate of helium and oxygen, and the open circuit potentials were measured at different P_{O2}.

(2) CO Oxidation

The mixture of helium, oxygen, and carbon monoxide was supplied to the reactor, maintaining the mean space time at about 0.12min. The reaction rates were

measured at the various P_{CO}/P_{O2} and temperatures under open circuit condition. The same experiments were carried out under polarization conditions. Namely, the overpotentials were applied to the platinum electrode by potentiostat for the purpose of observing the change in the reaction rates with the overpotentials; i.e. the NEMCA effect. For a specific overpotential given, we have measured the current across the electrolyte was measured by the potentiostat and the composition of the product, was analyzed by on-line gas chromatography (HP, 5890 II).

3. Results and Discussion

3.1. Under Open Circuit Condition

(1) Open Circuit Potential

On the electrodes where oxygen is present, oxygen exchange reaction occurs.

$$O_2 + 4e^- \Leftrightarrow 2O^{2-} \qquad (6)$$

When oxygen exchange reaction is dominant on the surface of electrodes and thermodynamic equilibrium is established between oxygen in the gas phase and that adsorbed on the electrode, then the Nernst equation can be used to calculate the open circuit potential between the working electrode where helium and oxygen are applied and the counter electrode which is exposed to ambient air,

$$E = \frac{RT}{nF} \ln \frac{P_{O2}(atm)}{0.21} \qquad (7)$$

If ln is replaced by log, then the slope is calculated to be about 38.4mV/decade (=2.3RT/nF). The theoretical open circuit potentials calculated by equation 7 (dotted line) are compared with the experimental data (solid circles) in Fig. 2 at the various oxygen pressures. Since the experimental data with the slope of 38.1mV/ decade agree well with the theoretical value, it can be assumed that no corrosion takes place under the experimental conditions (temperature, oxygen pressure).

If CO is added to the mixture of helium and oxygen, the potential which is different from Eqn. (7) is formed. The new potential is called a mixed potential [10] and it is ascribed to the following CO oxidation electrochemical reaction in addition to oxygen exchange reaction.

(2) CO Oxidation

Conversions and reaction rates at the various reactant compositions under open circuit condition are represented in Fig. 3. Conversions and reaction rates of CO oxidation were measured at the various ratios of the inlet CO partial pressure to

the inlet O_2 partial pressure, P_{CO}/P_{O2}, with $P_{CO}+P_{O2}$ being fixed at 0.02 atm, and at the temperature of 500℃. It is seen from Fig. 3 that as P_{CO}/P_{O2} increases, the reaction rate decreases in the experimental ranges studied. It is because the surface of the catalyst is covered with CO which inhibits the adsorption of O_2 and thus the oxidation reaction. The above observations can be expressed in the following relationship [14].

$$r = (k_1 P_{O2})/(KP_{CO}) = k(P_{CO}/P_{O2})^{-1} \quad (8)$$

where k_1 is the rate constant for molecule O_2 adsorption, K is the equilibrium constant for CO adsorption, and k is a lumped constant, k_1/K. From the experimental data, k is estimated to be about -1.946×10^{6} mol/min.

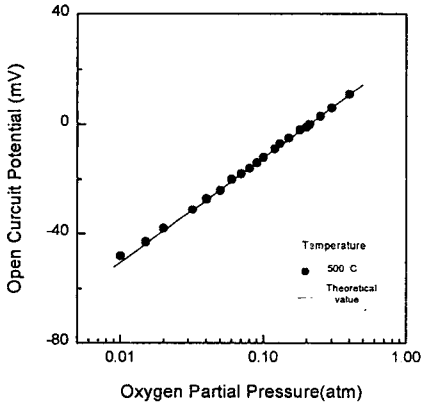


Fig. 2. Open circuit potentials with the oxygen pressure.

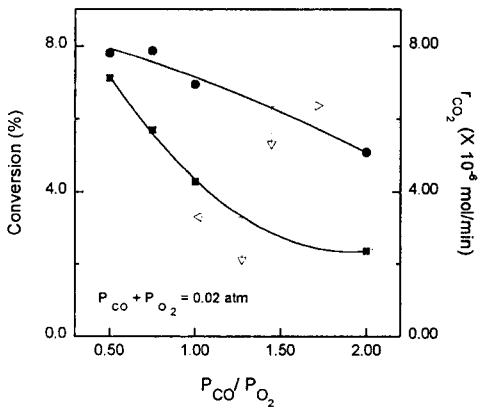


Fig. 3. Effect of P_{CO}/P_{O2} on conversion and reaction rates at T=500℃.

In the CO oxidation, which follows the Langmuir-Hishelwood model [15], the rate-determining step has been considered to be the formation of CO_2 activated complex through the reaction between mobile CO molecules on the surface and chemisorbed oxygen atoms, and thus the reaction rate strongly depends on the breakage of carbon bond of CO from the metal. The linear correlation of the surface reaction activation energy, E, with the heat of adsorption of CO, Hco, implies that the formation of such an activated complex involves the breaking of the metal-carbon bond of the adsorbed CO. Therefore, the barrier to formation of the activated complex is the barrier encountered when CO is moved on top of a chemisorbed oxygen atom. The activation energy was calculated to be about 6.6 kcal/mol from Arrhenius plot in Fig. 4, and this value falls in the range of reported values, 6.4 kcal/mol [16], 12.0 kcal/mol [17].

3.2. Under Potentiostatic Operation

When a voltage is potentiostatically applied between the working and counter electrode, a current will flow, and the relationship between the current and the potential can be expressed by the Buttler-Volmer equation.

$$I = \pm I_0 \exp[\pm \frac{\alpha F(V_{WR} - V^{o}_{WR})}{RT}] \quad (9)$$

where I_0 is the exchange current density, α is the anodic and cathodic transfer coefficients, and V_{WR}^{0} is the catalyst(W) potential with respect to a reference electrode(R) under open circuit condition.

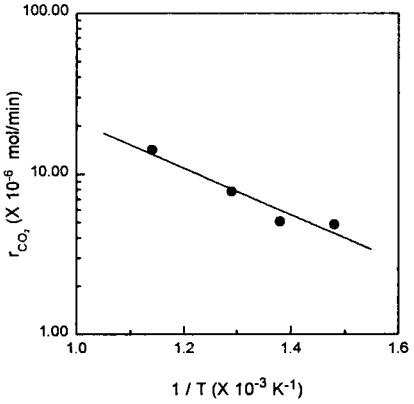


Fig. 4. Arrhenius plot of the reaction rates

When the mixture of He, CO and O_2 is supplied to the working electrode located inside of the reactor and a potential is applied between the working and counter electrode, then the NEMCA phenomena occur. It is divided into anodic polarization and cathodic polarization according to the potential direction. When anions are supplied onto the catalytic surface across the solid electrolyte, the anodic polarization is formed; whereas, when anions are removed from the catalytic surface, the cathodic polarization occurs. Under the NEMCA condition, the dependence of the catalytic reaction rate on the overpotential is expressed as [10]

$$r = r_0 \exp[\frac{\alpha F(\eta - \eta^{*})}{RT}] \quad (12)$$

where α and η are transfer coefficient and overpotential. After conversions and reaction rates were measured under open circuit condition, the change in conversions and reaction rates were measured as the overpotential varied.

The effect of overpotentials on the enhancement ratio at the various P_{CO}/P_{O2} is represented again in Fig. 5, when $P_{CO}+P_{O2}$=0.02 atm, P_{CO}/P_{O2} = 0.5 and T=500℃.

The enhancement factor for anodic polarization is greater than 1 with a maximum value of 37.1 at +300mV, implying that the oxidation rate has been increased through the promoted catalytic activity. When CO and O_2 are adsorbed on the surface of the working electrode according to the Langmuir-Hinshelwood model [15] in CO oxidation, the strong $Pt-O_{(a)}$ or $Pt-CO_{(a)}$ bond will be formed ; therefore, breakage of such a bond becomes the rate controlling step. Since O^2 ions supplied to catalyst electrode increase work function under anodic polarization, the $Pt-CO_{(a)}$ and $Pt-O_{(a)}$ bonds are weakened and the reaction rate increases with increasing reactivity of $CO_{(a)}$ and $O_{(a)}$. However, it is clearly seen from Fig. 5 that the NEMCA effect is dominant at lower anodic overpotentials; whereas the faradaic electrochemical oxidation due to high current prevails at higher anodic over- potentials. Therefore, the maximum reaction rate or the maximum enhancement ratio ($\rho = r/r_0$) of 2.70 appears at +900mV, where both the NEMCA effect and the faradaic electrochemical reactions are important.

It is also seen from Fig. 5 that Λ values are almost constant at about 16, and ρ values are less than 1 under cathodic polarization. This is because the coupling between $CO_{(a)}$ or $O_{(a)}$ and the catalyst surface becomes strong under cathodic polarization, resulting in the decreased reaction rate. In this case, therefore, the NEMCA effect is dominant compared with the faradaic electrochemical reaction, and affects CO oxidation in such a way that the reaction rate is lowered. This is also confirmed from the fact that a small amount of current flowed over the entire range of the cathodic overpotential. With such a small amount of current, the increase in the reaction rates through the faradaic electrochemical reaction could not be observed.

Fig. 6 shows the effect of P_{CO}/P_{O2} on the enhancement factor and enhancement ratio at two different overpotentials of +300mV and -300mV when $P_{CO}+P_{O2}$ =0.02atm and T=500℃. For comparison the open circuit case is included in the figure. It is seen from Fig. 6 that Λ increases regardless of the overpotentials as P_{CO}/P_{O2} decreases, implying that the NEMCA effect prevails at the lower range of P_{CO}/P_{O2} where oxygen molecules are abundant. ρ also becomes larger than 1 under anodic polarization and less than under cathodic polarization because of such a NEMCA effect. If the partial pressure of oxygen in the reactor is high, and thus the oxygen coverage is high, the amount of oxygen which forms CO_2 activated complex with adsorbed CO will increase. The NEMCA effect induced by the application of the anodic polarization is maximized at higher P_{O2}, or at lower P_{CO}/P_{O2}. Under cathodic polarization the reaction rate decreases due to the increased bonding strength of the adsorbed species on the catalytic surface, but degree of such effect at lower P_{CO}/P_{O2} is not so much as the case under anodic

polarization.

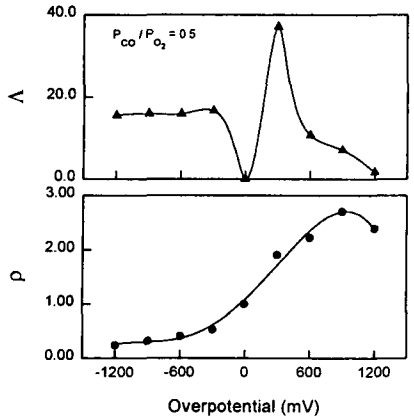


Fig. 5. Effect of overpotential on ρ and Λ at the various P_{CO}/P_{O2}.

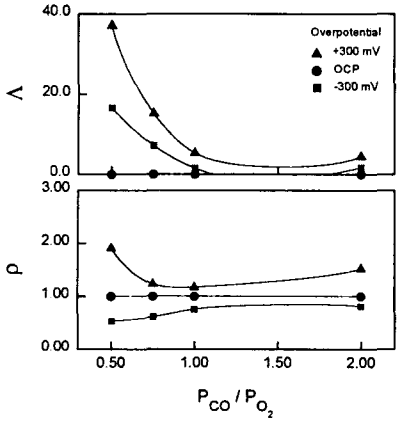


Fig. 6. Effect of P_{CO}/P_{O2} on ρ and Λ at the various overpotentials.

4. CONCLUSION

Electrochemical promotion of the reaction rate was investigated for CO oxidation in a solid electrolyte catalytic reactor. Before a voltage was applied, oxygen exchange reaction for the He-O_2 system was studied and it was found that the open circuit potential between the working electrode and the counter electrode exactly followed the Nernst equation. The open circuit potential for the He-O_2-CO system showed a mixed potential of O_2 exchange reaction and other electrochemical reaction induced by CO.

When the circuit was closed and the overpotentials were applied to the working electrode, the reaction rates of CO oxidation were found to increase or decrease non-faradaically, namely, not proportially to the O^2 ion passing rate through the electrolyte according to the current direction. r/r_0 increased up to 2.70 under anodic polarization; whereas decreased down to 0.24 under cathodic polarization. This is because the bonding strength of the adsorbed species on the electrode surface weakens under anodic polarization and increases under cathodic polarization.

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