

The Corrosion Behavior of Li/K Carbonate Melts with CaCO₃ Additives on Separator Plate in the Molten Carbonate Fuel Cell in the Anode Environments

† Kyehyun Cho, Chul-Hwan Lee, and Zu-Hwan Sung

*School of Materials Science Engineering, Yeungnam University
Kyongsan, Kyongbuk, Korea*

High temperature corrosion behavior of AISI-type 316L stainless steel for the MCFC(molten carbonate fuel cell) bipolar application was studied by immersion test and penetration attack method in anode environment (650 °C, Li₂CO₃/K₂CO₃ =62/38 mol%, H₂/CO₂=80/20 vol%) without or with different CaCO₃ content. Not only immersion test method but also morphological observation of samples in the carbonate melts are adopted as experimental methods. With aid of the morphological observation of cross section of samples immersed in a carbonate melt was possible to obtain penetration attack.

The concentration effect of CaCO₃ inhibitor was investigated in order to verify the optimum concentration for practical application in MCFC stack operation. The corrosion rate in the presence of CaCO₃ was proven to be decreased as a function of CaCO₃ concentration. The corrosion rate in the presence of CaCO₃ was measured with a value of 6.9 mpy which is 2.4 times lower than that of inhibitor-free electrolyte.

The cross section microscopy revealed that the internal penetration by oxidation in molten carbonate is very severe. In this case, the attack was occurred not only dissolution loss in the electrolyte by corrosion reaction but also weight gain through oxide layer by internal penetration.

Keywords : molten carbonate fuel cell, separator plate, inhibitor, Ca additives

1. Introduction

The fuel cell is spotlighted as a friendly environmental alternative energy. It can be generally divided into Alkaline Fuel Cell, Phosphoric Acid Fuel Cell, Molten Carbonate Fuel Cell(MCFC), Solid Oxide Fuel Cell, and Polymer Electrolyte Fuel Cell according to an applied electrolyte. Molten Carbonate Fuel Cell so called new second generation fuel cell, because operated in high temperature 650 °C, have good points of which can cause fast electrochemical reaction without use of expensive platinum catalyst and is able to utilize high waste heat such as Phosphoric Acid Fuel Cell.¹⁾ Also, since it can be fueled carbon monoxide as well as hydrogen, pre-treatment process of MCFC is more simple, and since its unit cell voltage is higher than that of Phosphoric Acid Fuel Cell, which is superior in respect to power efficiency. It will be considerably expected that MCFC will be commercialized as future energy device constituting high efficient complex power system including gasification of

coal process and the MCFC system.²⁾

Molten carbonate fuel cell has high corrosivity environments due to high temperature operation, which provokes corrosion of separator and lowering of capacity. Also, in order to make possible to operate MCFC during 40,000 hours which is the target for commercialization, safety and dependence of cell should be improved through improving durability of Separator plate. The separator plate in molten carbonate fuel cell plays a role dividing between anode and cathode, coupling electric current with an exterior circuit, and supplying a channel of reacting gas.³⁾ This separator takes great expenditure among fuel cell's structural elements. When stacked up with unit cell, the separator plate have some problems such as high temperature salt corrosion at both side of anode and cathode because it is inserted between each unit cells and put in high temperature molten carbonate electrolyte and anode reducing gas and cathode oxidizing gas atmosphere.

In order to choose for good corrosion inhibitor, carbonate type should be selected as alternatives to minimize effects on electrolyte. Among them, it was to some degree reported⁴⁾ that alkaline earth carbonate have an some

† Corresponding author: khcho@yu.ac.kr

slightly working on oxidation of high temperature material for structural elements such as restraint of oxide formation and AISI-type stainless steel weight loss. Thus, CaCO₃ was used as candidate corrosion inhibitor.

Thus, to investigate decreasing corrosion rate for separator plate in MCFC, this paper is focused on change of electrolyte composition in molten carbonate fuel cell at anode atmosphere to develop a proper corrosion inhibitor.

2. Experimental

The corrosion test for separator plates in molten carbonate fuel cell have been applied with numerous methods, reliability of test results appears different from analysis of instrumentation along with each purpose decided by experimental plan, so its reproducibility is fairly important. Measurement and study about corrosion of molten carbonate fuel cell generally uses electrochemical techniques utilizing traditional three electrode system and a way of measurement of weight loss by immersion, and except both, simulated test, etc. can be applied to the test by each environment.⁵⁾⁻⁷⁾

In this experiment, AISI-type 316L, material of separator plate, having excellent corrosion resistive material in aqueous environment, is implemented for immersion and electrochemical test at reduction environment of molten carbonate fuel cell, high corrosive atmosphere, (anode :650 °C, Li₂CO₃/K₂CO₃ = 62/38 mol %, H₂/CO₂ = 80/20 vol%).

The specimen was regularly cut in dimension of 2 cm×2 cm×0.1 cm. And to remove grease and grime, the samples was washed in distilled water followed by Ultrasonic cleaner in acetone during 30 minutes, finally treated with methanols. The samples were polished with from 200 grit sand paper to 0.3 μm alumina powder. To obtain reproducible result, specimen were carried out with heating treatment. The heat treatment processes are as follows; they were vacuumed in quartz tube after wrapped into quartz wool, and went though the solution treatment up to 1,200 °C for 4 hours, next water quenched for rapidly quenching samples during heating treatment. Throughout these process, by protecting defect and work hardening of metal by mechanical working, sensitization of stainless steel can be prevented and specimen can be uniform composition as shown in Table 1 for AISI-type 316L stainless steel.

Immersion test is a method which evaluate weight loss of sample after and before experiment. The experimental set-up consists of a cylinder type pot call as shown in Fig. 1.⁸⁾ It consists bath of a high purity alumina crucible

Table 1. Chemical Compositions of the AISI type 316L austenitic stainless steel

AISI grade	Weight % (Fe balance)							
	Cr	Ni	C	Mn	Si	P	S	other
316	16-18	10-14	0.08	2.0	1.0	0.045	0.030	Mo: 2.0-3.0
316L	16-18	10-14	0.03	2.0	1.0	0.045	0.030	Mo: 2.0-3.0

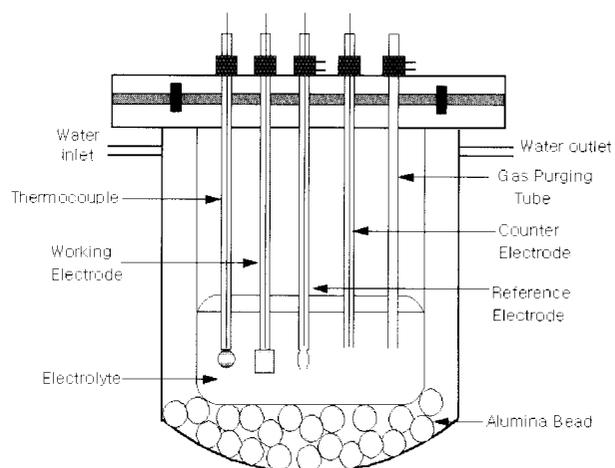


Fig. 1. Schematic pot-cell set-up for the experiment

which is enclosed by double wall stainless steel of autoclave type crucible. It was sealed with gas at the uppers part, and the upper part of this autoclave crucible has a water cooling jacket protecting fragile components from heating, Additionally, It contains thermocouple for controlling temperature and bubbler for purging gas.

All specimens quantified before test was put in alumina crucible with well mixed eutectic electrolyte Li₂CO₃ and K₂CO₃, sealed and heated to 650 °C for 5 hour at reduction atmosphere of molten carbonate fuel cell, the highest corrosion environment, (anode: 650 °C Li₂CO₃ / K₂CO₃ = 62/38 mol%, H₂/CO₂ = 80/20 vol%), and CaCO₃ was used as candidate corrosion inhibitor. After immersion test, the samples were washed in ultrasonic for removing coagulated carbonate and impurities adhered to surface, and weighed. On the order hand, surface cleaning method was adopted the following washing method⁹⁾ that 1) boil specimens in 18% NaOH + 3% KMnO₄ solution for 4 hours, 2) wash with distilled water, 3) soak them in 10% citric acid ammonium solution during a few minutes, 4) rinse with acetone. Since this method uses acid and alkali solution. Corrosion products and metal surface should be not to be oxidized or eroded by acid and alkali solution, thus it should be cautious of carrying out this method.

After calculating corrosion rate of weight loss, cross-section observation is necessary to calculate corrosion rate by oxidation, so to determine corrosion rate and analyze

corrosion characteristics, the surface and the cross-section of the sample with change of layers suffering from corrosion were observed using SEM(Scanning Electron Microscopy, Hitachi S-400) and optical microscopy.

4. Results and discussion

To measure the basic corrosion rate at the anode atmosphere of MCFC, H₂/CO₂ (80/20 vol%) and Li₂CO₃/K₂CO₃(62/38) eutectic electrolyte, immersion test was carried out without CaCO₃ content during 24 hours. The obtained results were adopted as standard corrosion rate in the absence of inhibitor. The test was worked out with adding CaCO₃, in the content of 1.2 wt%, 2.4 wt%, 5 wt%, and 10 wt%, others are in same conditions. The corrosion rate was calculated in mpy(mils penetration per year) as shown Table 2 with measuring weight loss and using equation as following,⁵⁾

$$mpy = \frac{534W}{DAT} \quad (1)$$

Table 2. Corrosion rate of AISI-type 316L with and without CaCO₃ inhibitor in MCFC anodic condition (H₂/CO₂ = 80/20 vol%, (Li_{0.62}K_{0.38})₂CO₃:additive = x:y wt%)

Atmosphere	Time (hr)	Corr. rate (mpy)
without inhibitor	24	17.876
without inhibitor	24	17.653
without inhibitor	24	15.195
1.2wt% CaCO ₃	24	20.558
2.4wt% CaCO ₃	24	14.301
5wt% CaCO ₃	24	8.491
10wt% CaCO ₃	24	6.927

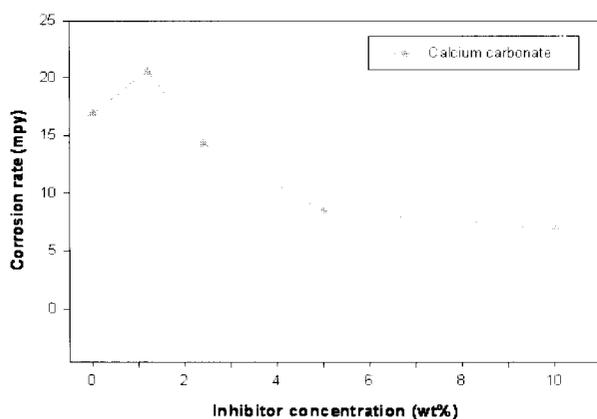
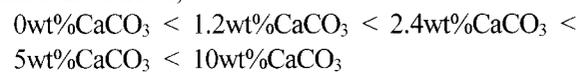


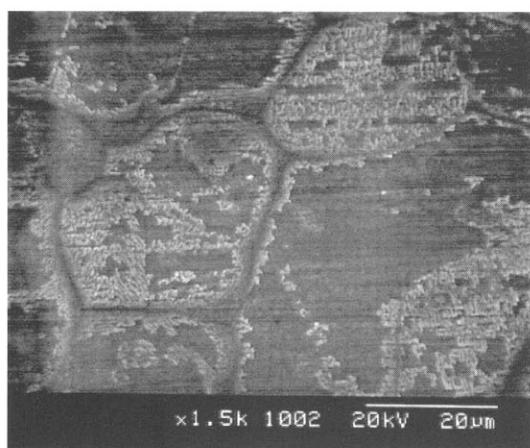
Fig. 2. The corrosion rate as a function CaCO₃ concentration in the carbonate melts of AISI-type 316L in MCFC anodic condition (H₂/CO₂ = 80/20 vol%)

W is weight loss(mg) of specimen, D is density(g/cm²) of specimen, A is a surface area(cm²), T is the time when specimen is deposited in corrosive electrolyte. In the corrosion experiment of MCFC, the corrosion rate can be expressed as the penetration rate by mils/year(mps). The penetration rate by weight loss measurement is easily calculated by data obtained from immersion experiment. It is most popular expression to use corrosion rate by permeation per unit time in all engineering aspects, but sometimes weight loss per unit area or unit time. Fig. 2 shows corrosion rate (mpy) on the basis of data obtained by weight loss method representing as a function of CaCO₃ concentration in the carbonate melts of AISI-type 316L in MCFC anodic condition (H₂/CO₂ = 80/20 vol%). The corrosion rate without inhibitors was represented to 17 mpy, average value of three results as shown in Table 2, which results is higher than that of cathode atmosphere about 13 mpy,¹⁰⁾ hence it is known that corrosion rate at anode atmosphere is higher than that of cathode atmosphere. The reason is that stable passive layer at cathode atmosphere can be produced by high activity of oxygen in the carbonate melts. The immersion test for 24 hours showed the corrosion resistance effect of corrosion inhibitors as follows;

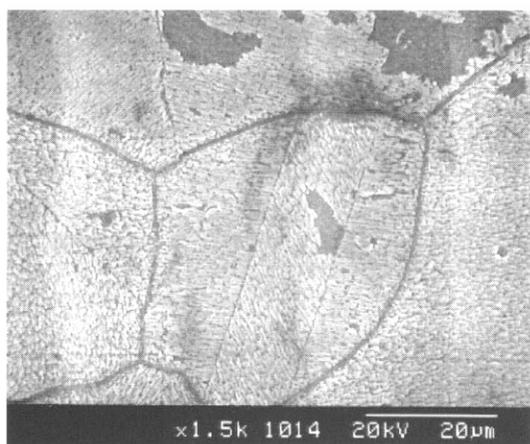


The relationship between the corrosion rate and composition CaCO₃ by weight loss method, the corrosion rate was decreased by an increase of concentration of additive for each CaCO₃ concentration. It is well known that inhibitors in the electrolyte behaved as different corrosion rate with concentration change. In case of passivator, it is reported¹¹⁾ that only above critical concentration, it plays a inhibition action role. However, below the concentration, it sometimes accelerates corrosion rate by local cell action such as pitting. At proper concentration, it makes effectually restoration action to maintain formation of strong oxide layers continuously. Also, it can be estimated that CaCO₃ in carbonate melt appear low corrosion resistance by reason that oxide film is unstable at low concentration since one has reported¹²⁾ that at oxide analysis experiment with adding CaCO₃ 10mol% and carbonated coating, Ca compound was not observed.

Previously, it was reported by M. Yanagida et al.¹²⁾⁻¹³⁾ that in addition of CaCO₃, the corrosion rate of AISI-316L stainless steel was measured. However, the effect of decreasing corrosion was slight with weight loss measurement inconsistent with this result. It is probably that experimental time and methods are different. Yanagida et al. utilized the test method such as thin coating 5 mg/cm² carbonate layer on the sample. It is reported that the



(a)



(b)

Fig. 3. SEM image of surface after 24 hours immersion test (a) without inhibitor (b) 1.2wt% CaCO_3

corrosion rate of AISI-type 316L and FA-ODS appear parabolic behavior^{13),14),15)} Also, the study was proven that in a case adding CaCO_3 to electrolyte melt, the weight gain curve appears the parabolic behavior with time. Also, the long time immersion test must be needed because the commercial time of MCFC is 40,000 hours.

Fig. 3 shows the SEM image of the surface after 24 hours immersion test (a) without inhibitor (b) 1.2 wt% CaCO_3 addition at 650 °C. The black lines between white spots in the grain boundary region are attack fairly high compared to other surface. Also, grain boundary on the surface(Fig 3a) in the absence of CaCO_3 addition in carbonate electrolyte was wider than that of CaCO_3 addition (Fig. 3b). In the addition CaCO_3 in the electrolyte, the white spots on the surface(Fig. 3b) is more abundant than that of inhibitor-free electrolyte (Fig. 3a) which implies that white spot acts as physical barrier for degradation in the MCFC anodic environments.

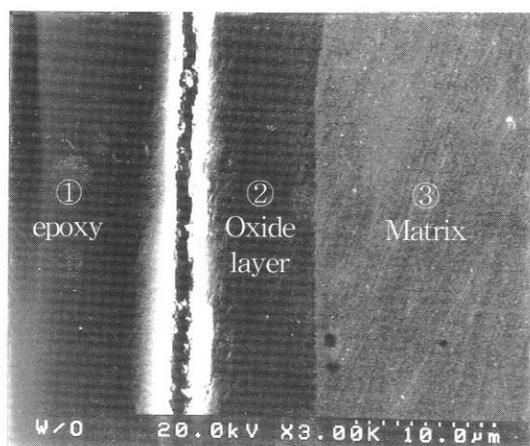
The corrosion regions are wet-seal parts which is inner surface of anode or cathode flange and current collector which is located in porous electrode surrounded by flange. The electrochemical reaction both oxidation reaction and metal dissolution reaction in molten carbonate fuel cell can be normally represented for the following equations (2)~(5) which can be applied to stainless steel as well as Fe, Ni and Cr.⁸⁾

Thus, at anode environment of MCFC separator plate, above electrochemical equations can be divided into two different type degradation; wight loss by electrolytic corrosion in which metal is directly dissolved and weight gain where oxidizing reaction occurs at interface between molten salt and metal. It is possible to know that weight loss of immersion test depends on dissolution reaction and formation of oxide layers progress with weight gain. Since oxidation reaction appears in weight gain between matrix and oxide layer, the rate caused by oxidizing reaction can be calculated with evaluation of cross-section on oxide layers from a interface thickness growth process. Hence, as above stated, as calculating the corrosion rate measured by weight loss is not solely for corrosion rate of MCFC separator. Instead, corrosion rate of material in molten carbonate melts should be added up by evaluation of the oxidation rate obtained by observation of cross-section on the sample with SEM.

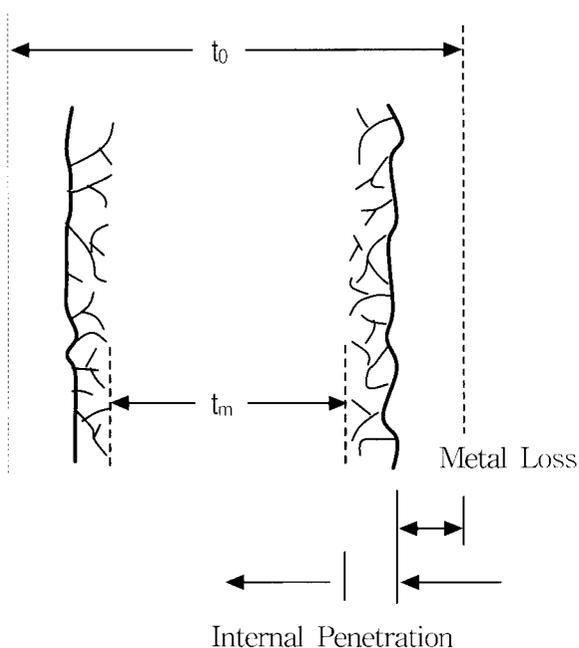
Fig. 4. shows SEM image of cross section after penetration attack(a) and schematic drawing of the metal loss for determining the total depth attack for metal loss and internal penetration(b) after 24 hours immersion test with corrosion inhibitor. Fig. 4a shows SEM cross-section photograph; ① is epoxy, ② is oxide layer, penetration depth by oxidation in carbonate melts, and ③ is matrix. The thickness of oxide layer on the micrograph is increases as a function of immersion time due to internal penetration. The evaluation methods for high temperature corrosion have been applied to weight loss or weight gain, but there are many problems to use it for high temperature oxidation and corrosion by salt because oxidation can depend material on surface with ingredient, density, or with or without oxide layers. As shown in Fig 4a, total depth attack should be considered both dissolution and corrosion when weight loss and weight gain takes place at same time on the same surface. A method determining total depth attack is represented in Fig. 4b as the following equation.¹⁶⁾

$$\text{Total depth attack (mm)} = \frac{t_0 - t_m}{2} \quad (2)$$

t_0 : thickness of specimen in initial
 t_m : remaining good metal



(a)



$$\text{Total depth attack (mm)} = \frac{t_0 - t_m}{2}$$

t_0 : original specimen distance
 t_m : remaining good metal

(b)

Fig. 4. SEM image of cross section after penetration attack(a) and schematic showing the total depth of attack method for degradation both metal loss and internal penetration(b)

Fig. 5. shows SEM cross section microscopy by performing immersion test in the Li/K carbonate melts after 24 hours.(a) 1.2 wt% CaCO₃, (b) 2.4 wt% CaCO₃, (c) 5 wt% CaCO₃, (d) 10 wt% CaCO₃. As shown in Fig 5a, the oxide layer between epoxy layer and matrix was very clearly observed with a 7.6 µm at 24 hours immersion test in the presence of 1.2 wt% CaCO₃, if not adding inhibitor, oxide layer was about 8.7 µm which indicates a part of

interface was retarded by oxidation in the presence of CaCO₃. Also, relatively dense oxide layers were formed as shown in Fig 5a, which are probably attributed to be dense and continuous film of Li-Fe/Cr oxide.¹⁷⁾ As an increase of CaCO₃ content with 2.4 wt%, 5 wt%, 10 wt%, the oxide layers became thinner for 6.7 µm, 8.0 µm, 5.4 µm, respectively. The thickness of oxide layer with 5 wt% CaCO₃ (Fig. 5c) was high, not as usual, in which the oxide layer formed with uniform, but with porous, as a result, oxide layer probably becomes thicker than 2.4 wt% one. The oxide layer 10 wt% CaCO₃ is much lower than that of the other composition. In the presence of CaCO₃, weight loss by dissolution is decreased significantly, however, thickness of oxide layers were not much decreased. It implies that inhibition action of CaCO₃ is different for dissolution and oxidation reaction. It is the reason that corrosion reaction by dissolution and oxidation reaction by internal penetration plays a different role on each different mechanism. Fig. 6 was plotted by the calculation based on oxide layer observation from Fig. 5. Fig. 6 demonstrates oxide thickness with concentration dependent of CaCO₃ after 24 hours immersion test in MCFC anodic condition (H₂/CO₂ = 80/20 vol%).

As shown in Fig. 5, in the presence of CaCO₃ high temperature oxidation behavior exhibited more shallow oxide layer than inhibitor-free electrolyte. From the various content of inhibitor, 10 wt% CaCO₃ forms the most thin layer and densest oxidation layers which are hindered from high temperature oxidation by CaO layer shown in Fig. 5a and 5b but several cracks in layers as shown in Fig. 5c and 5d.

After immersion test in the pot cell in the molten carbonate melts, cross section observation was made by SEM. It was obvious that internal penetration appear in the oxide/matrix interface, therefore, it is necessary to interpret total depth attack for degradation rate as mentioned above on Fig. 4b. The total corrosion rate will be evaluated as the following; in the presence of CaCO₃ in the molten carbonate melts on AISI-type 316L, firstly the corrosion rate by weight loss can be calculated with mpy, secondly oxidation rate by internal penetration can be evaluated with SEM oxide layer. The total corrosion rate(mpy) at molten carbonate fuel cell can be expressed by summing both calculated values which are obtained by weight loss and by measuring oxide layers thickness on the cross section SEM microscopic images. Therefore, total depth attack should be summed both corrosion rate (Fig. 2) and oxidation rate (Fig. 6) Fig. 7 demonstrates total corrosion rate with different concentration of CaCO₃ inhibitor after 24 hours immersion test in MCFC anodic condition(H₂/CO₂ = 80/20 vol%) As shown in Table 3, the

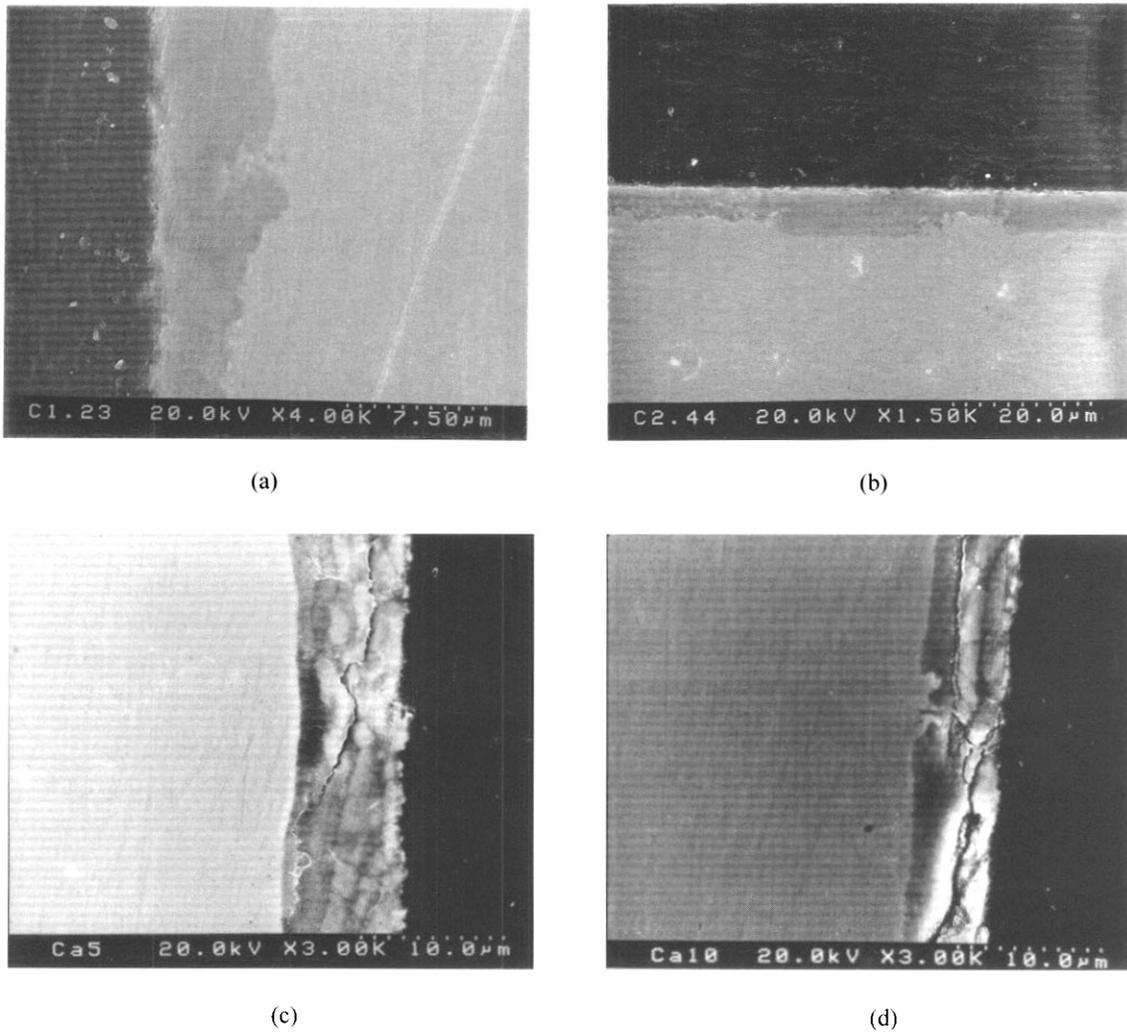


Fig. 5. SEM image of cross section after 24 hours immersion test for different additive. (a) 1.2wt% CaCO_3 , (b) 2.4wt% CaCO_3 , (c) 5wt% CaCO_3 , (d) 10wt% CaCO_3

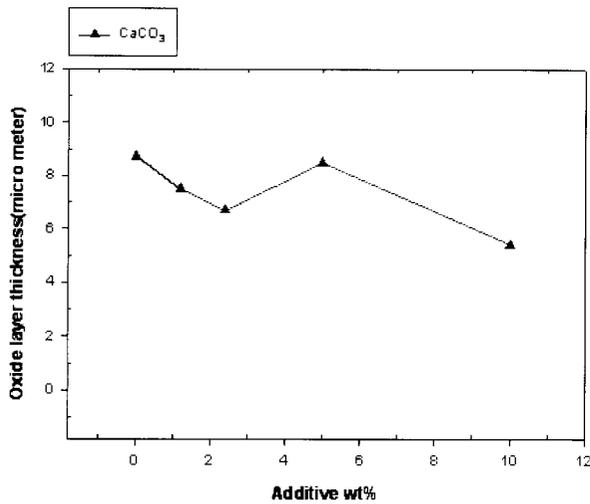


Fig. 6. Change of oxide thickness with different concentration of CaCO_3 after 24 hours immersion test in MCFC anodic condition. ($\text{H}_2/\text{CO}_2 = 80/20$ vol%)

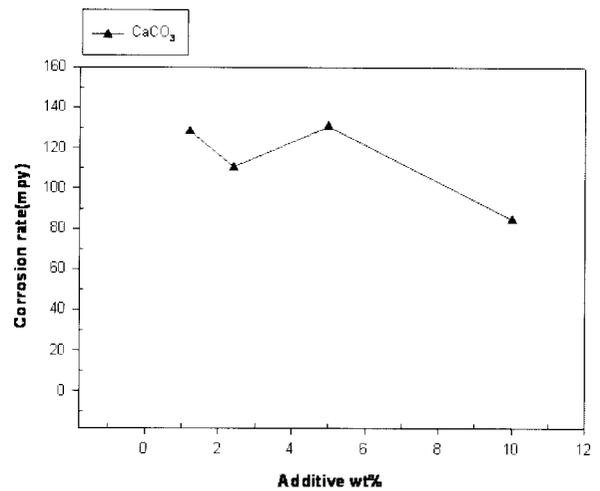


Fig. 7. Total corrosion rate with different concentration of CaCO_3 inhibitor after 24 hours immersion test in MCFC anodic condition ($\text{H}_2/\text{CO}_2 = 80/20$ vol%)

Table 3. Total corrosion rate after immersion test for 24 hours (weight loss + oxide thickness on cross section)

Concentration	Additive	Corrosion rate (mpy)	
		CaCO ₃	without inhibitor
1.2 %		128.38	141.92
2.4 %		110.58	
5 %		130.64	
10 %		84.53	

total corrosion rate at 24 hours immersion test for 1.2 wt%, 2.4 wt%, 5 wt%, 10% CaCO₃ was evaluated the value of 128.38 mpy, 110.58 mpy, 130.64 mpy, 84.53 mpy, respectively. However, Cho, et al.⁸⁾ who recently studied corrosion mechanism at oxidizing atmosphere with sensitized AISI-type 316L in solution as well as molten carbonate reported⁸⁾⁻¹⁰⁾ that first intergranular corrosion make very small groove and it is very sensitive to initiation of local attack. In case of 5 wt% CaCO₃, the surface was probably attacked by local cell action thereby exhibit sudden increase of oxidation rate. Since corrosion of separator plate of molten carbonate fuel cell appeared in various environments and conditions, several method¹⁷⁾⁻²⁰⁾ for evaluation of corrosion have been implemented. Yet, accurate data have been produced, so it is necessary that reasonable experimental methods should be adopted as standard method to breakthrough for commercialization of MCFC. In this paper, we propose new evaluation of the corrosion rate after immersion test in molten carbonate fuel cell anode environments by total measurement method.

4. Conclusion

In order to investigate the basic corrosion behavior of AISI-type 316L at anode atmosphere, H₂/CO₂(80/20 vol%) of MCFC in electrolyte Li₂CO₃/K₂CO₃ (62/38 mol%), using electrolyte without corrosion inhibitor, the corrosion behavior was performed. Corrosion behavior not only dissolution of separator in the carbonate melts but also internal penetration by oxidation attack were measured and observed as a function of CaCO₃ composition. With aid of the morphological observation of cross section of samples immersed in a carbonate melt with various additive was possible to obtain penetration attack.

The total corrosion rate of separator plate of MCFC in the presence of CaCO₃ was evaluated as a value of 6.9 mpy which is 2.4 times lower than that of inhibitor-free electrolyte. The CaCO₃ is good inhibitor comparing with the condition without inhibitors up to 100 hours immersion

test.

Corrosion behavior of MCFC anodic environments reveals two types of degradation as follows: high temperature oxidation by inner penetration depth and corrosion by dissolution in the melts. Therefore, it is more reasonable that the total corrosion rate should be summed the corrosion rate by weight loss and the oxide thickness by internal penetration.

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