

Quantification of carbon dioxide poisoning in air breathing alkaline fuel cells

A. Tewari^{a,**}, V. Sambhy^b, M. Urquidi Macdonald^{a,*}, A. Sen^b

^a Department of Engineering Science and Mechanics, Pennsylvania State University, PA 16802, USA

^b Department of Chemistry, Pennsylvania State University, PA 16802, USA

Received 4 January 2005; accepted 7 March 2005

Available online 6 July 2005

Abstract

Carbon dioxide intolerance has impeded the development of alkaline fuel cells as an alternate source of power supply. The CO₂, in a fuel cell system, could come from the anode side (if “dirty” H₂ is used as fuel), from the cathode side (if air instead of pure O₂ is used as an oxidant) or from inside the electrolyte (if methanol is used as a fuel). In this work, an novel analytical approach is proposed to study and quantify the carbon dioxide poisoning problem. Accelerated tests were carried out in an alkaline fuel cell using methanol as a fuel with different electrical loads and varying the concentration of carbon dioxide in a mixture CO₂/O₂ used as oxidant. Two characteristic quantities, t_{\max} and R_{\max} , were specified which were shown to comprehensively define the nature and extent of carbon dioxide poisoning in alkaline fuel cells. The poisoning phenomenon was successfully quantified by determining the dependence of these characteristic quantities on the operating parameters, viz. atmospheric carbon dioxide concentration and applied electrical load. Such quantification enabled the prediction of the output of a fuel cell operating in a carbon dioxide enriched atmosphere. In addition, static and dynamic analyses of electrolytes were carried out to determine the dependence of cell current on the electrolyte composition in a fuel cell undergoing poisoning. It was observed that there is a critical concentration of KOH in the electrolyte only below which the effect of carbon dioxide poisoning is reflected on the cell performance. Potentiostatic polarization tests confirmed that the underlying reason for the decreased cell performance because of carbon dioxide poisoning is the sluggish kinetics of methanol oxidation in the presence of potassium carbonate in the electrolyte. Moreover, the decreased conductivity of the electrolyte resulting from hydroxide to carbonate conversion was also shown to increase the ohmic losses in an alkaline fuel cell leading to lower efficiencies.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Alkaline fuel cells; Carbon dioxide poisoning; Accelerated carbon dioxide poisoning tests; Quantification of carbon dioxide poisoning; AFC

1. Introduction

Alkaline fuel cells (AFC) are an attractive, non-conventional source of energy. AFC offer several advantages over the more commonly used and researched PEMFC. The kinetics of the electrode reactions are superior in an alkaline environment (AFC) compared to acidic environment (PEMFC) [1–4,15]. The inherently faster kinetics of the reac-

tions in an alkaline fuel cell allows the use of non-noble metal electro-catalysts like nickel, silver, etc. [5–8]. AFC also exhibit much higher current densities and electrochemical efficiencies at comparable temperatures over PEMFC. In addition, the liquid KOH electrolyte used in AFC is much cheaper than the polymer electrolyte (nafion) used in PEMFC, which need constant humidification for proper functioning [9]. Water management is also not a major issue with AFC as with PEMFC, thus allowing simplicity in design and fabrication. AFC can be operated at a higher temperature (100–120 °C), thereby using the Arrhenius effect to the advantage and, hence, obtaining higher efficiencies. PEMFC cannot be operated above 90 °C due to problems with the

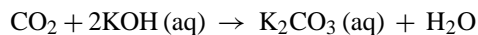
* Corresponding author. Tel.: +1 814 863 4217.

** Co-corresponding author. Tel.: +1 814 777 2887.

E-mail addresses: mumesm@engr.psu.edu (M. Urquidi Macdonald), axt227@psu.edu (A. Tewari).

hydration of the nafion membrane. Moreover, AFC electrodes are stable and not prone to the poisoning caused by carbon monoxide (CO), which poisons the platinum catalyst of the PEMFC [9]. Therefore, considering the cost and the simplicity of operation, AFC are more advantageous as compared to PEMFC and have better prospects in the commercialization of fuel cells.

However, AFC are inherently plagued by the problem of carbon dioxide poisoning, which limits their use as air-breathing energy sources. The poisoning reaction depletes the alkaline KOH electrolyte directly by the following reaction [10–12]:



This reaction has the effect of reducing the number of hydroxyl ions available for reaction at the electrodes. This conversion from hydroxide to carbonate also reduces the ionic conductivity of the electrolyte solution. In a very concentrated electrolyte solution, it may also have the effect of blocking the pores of the gas diffusion layer (GDL) by the precipitation of K_2CO_3 salt [13]. However, Gülzow and Schulze reported that, although carbon dioxide poisoning decreases an AFC performance, it does not cause any degradation of the electrodes [14]. Even after thousands of hours of operation in a carbon dioxide rich atmosphere, no additional electrode degradation, like deposition of K_2CO_3 , was observed. Al-Saleh et al. also showed the similar affect of carbon dioxide on a fuel cell performance [10]. It was observed that concentrations of up to 1% carbon dioxide in the oxidant stream of Ag/PTFE electrodes did not affect the cell performance over a period of 200 h.

Therefore, the most probable reason for the decrease in the cell performance is the change in electrolyte composition. Conversion of the electrolyte, from KOH to K_2CO_3 , by the absorption of carbon dioxide slows down the rate of oxidation of fuel at the anode [15,16]. The sluggish anode kinetics decreases the performance of a fuel cell as a whole unless the electrolyte is being circulated continuously. In addition, decreased electrolyte conductivity also increases the ohmic polarization leading to lower cell efficiency. Although the harmful effects of carbon dioxide poisoning can be partly reduced by circulating the electrolyte as discussed by Cifrain and Kordesch [17], a permanent solution is sought after to increase the possibility of AFC commercialization.

Several strategies have been proposed to counteract the carbon dioxide poisoning problem. Kordesch et al. mentioned that removal of carbon dioxide from air can be accomplished by chemical absorption of carbon dioxide by soda lime [12,17]. Molecular sieves were also suggested to be useful for carbon dioxide removal [18] but the requirement of dry air makes them inefficient. Ahuja and Green proposed an interesting strategy for carbon dioxide management, which involves the possibility of using liquid hydrogen to condense carbon dioxide out of the air [19,20]. Development of a solid anionic membrane would eliminate the problem of carbon dioxide problem as discussed [21–23]. Nevertheless, most

of the current strategies for solving the CO_2 poisoning issue in AFC are inadequate for commercialization. The inadequacy of current methods can be largely attributed to the lack of comprehensive studies on the carbon dioxide poisoning problem. Thus, our aim is to do a methodical quantification study of carbon dioxide poisoning in AFC.

One of the major handicaps in studying and quantifying the CO_2 poisoning in AFC is the length of time it takes to manifest when the cell is operated in ambient atmosphere. This is because air has only 0.03% CO_2 and, hence, the process of poisoning is very slow. Typically a cell had to be run for several hundreds of hours before the poisoning effect could be studied and quantified. Hence, a quick and efficient method to study and quantify the poisoning effect is desirable for developing effective remediation measures.

In this paper, we describe a method to study and quantify the carbon dioxide poisoning effect in AFC with a non-circulating electrolyte under conditions of accelerated poisoning by operating a fuel cell in an atmosphere enriched with carbon dioxide. Using this method, the carbon dioxide poisoning can be completely measured and studied in 2–5 h, depending on the percentage of carbon dioxide in the atmosphere. We have defined two variable parameters, t_{max} and R_{max} , which precisely describe the onset and the magnitude of carbon dioxide poisoning in AFC. These parameters can accurately and reproducibly predict the poisoning effect in AFC under different operating conditions. Therefore, these two parameters would act as important benchmarks while highlighting even small improvements in a cell performance when some carbon dioxide management strategy is employed. Consequently, efficacy of a method (like changing electrode catalyst or using filtration systems for carbon dioxide removal) to decrease the carbon dioxide poisoning can be determined on the basis of these benchmarks.

We have also investigated the effect of electrolyte composition on the performance of AFC. We have described how the current output of a cell varies with the changes in electrolyte composition during the poisoning process. To understand the relationship between the cell current and electrolyte composition, we carried out dynamic and static analyses of the electrolyte in an operational fuel cell. Potentiostatic polarization studies were also carried out to understand the underlying electrochemical basis of the carbon dioxide poisoning effect.

2. Experimental

2.1. Accelerated CO_2 poisoning studies

Small alkaline fuel cells operating on methanol as a fuel were purchased from the Department of Chemistry at The University of Hong Kong (Model # HKU-002C). The cathode was an AC-65 air cathode manufactured by Alupower Inc. [24]. The anode was fabricated on a nickel foam mat with a mixture of Pt/Co/Ni catalyst for methanol oxidation. The area of the anode was 18 cm^2 as compared to 10 cm^2 of

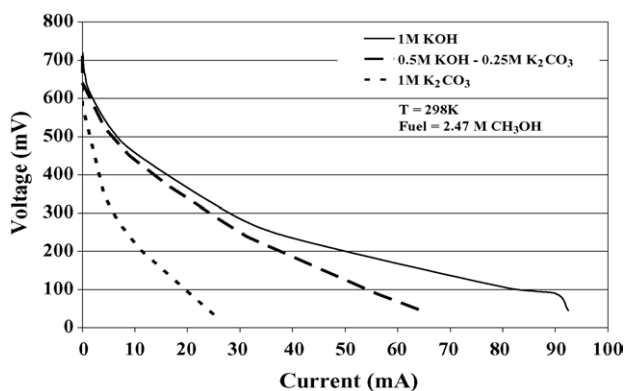


Fig. 1. Polarization curves of the fuel cells (HKU-002C) with different electrolytes at 298 K.

the cathode. The anode and cathode are separated by approximately 0.8 cm of an alkaline electrolyte. The cell body was made of plexiglass, which can be hermetically sealed during operation. The fuel cells were soaked with deionized water for 24 h prior to each cell run in order to ensure that the air cathode had been properly soaked and wetted so as to maximize the active area for electrochemical reactions. For each cell run, a mixture of 30 ml of 1 M potassium hydroxide (purchased from Aldrich) and 3 ml of 99.8% anhydrous methanol (purchased from Aldrich) was used as the electrolyte. The amount of methanol added was equivalent to a concentration value of 2.47 M. Fig. 1 shows the polarization curves of these fuel cells with three different electrolyte compositions. We notice that as the K_2CO_3 concentration increases in the electrolyte, both activation polarization and ohmic polarization increase, resulting in lower current output at a given voltage.

For operating the fuel cell in atmospheres with different concentrations of oxygen and carbon dioxide, an airtight plexiglass chamber was designed in which the cell could be placed and operated. A schematic of our experimental setup is shown in Fig. 2. The chamber had an inlet for the gases mixed in different ratios and was maintained at a slightly positive pressure by dipping the outlet in 2 cm of water. This was done to prevent any gases in the atmosphere from leaking inside.

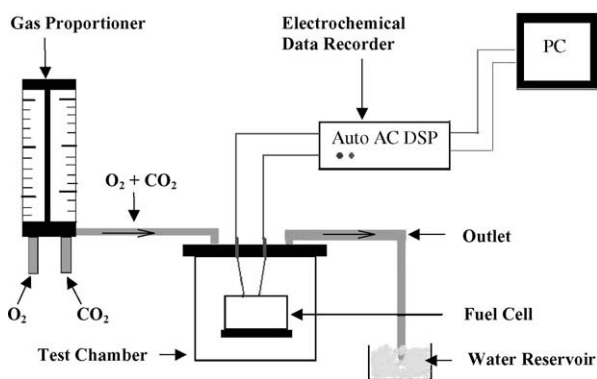


Fig. 2. Schematic of the experimental setup used for accelerated CO_2 poisoning experiments.

Appropriate metal contacts were provided so the cell could be connected to an external load and an electrochemical data recorder which was placed outside. Oxygen and carbon dioxide were mixed in different ratios using a gas proportioner, model no. 7951-4-4, obtained from Specialty Gas Equipment (OH). The gas proportioner was capable of mixing gases in any proportion with an accuracy of 1–2%. Different mixtures of oxygen and carbon dioxide (99.99% purity purchased from MG Industries, PA) were introduced into the test chamber with the fuel cell operating inside. A load of known resistance was applied across the fuel cell and an electrochemical data recorder, Auto AC DSP purchased from ACM Instruments (UK), was used to measure and record the cell current for approximately 5 h at an interval of 4 s each.

Cell runs with carbon dioxide levels in the atmosphere at 5%, 15%, 25%, 30%, 50% and 80% were carried out as described above. For every atmospheric composition, external loads of 1.3 Ω , 2.8 Ω , 5.2 Ω and 10.2 Ω were applied and the cell current was recorded. In this way, we generated a library of the fuel cell performances in different atmospheres and with different applied loads.

2.2. Electrolyte analysis

In static electrolyte analysis, samples of the electrolyte reflecting the change in electrolyte composition with the progress of the CO_2 poisoning in a fuel cell were made by mixing KOH (aq) and K_2CO_3 (aq) in different quantities. The chemical equation of the electrolyte degradation is given by the equation $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$. Therefore, to simulate the compositional changes of the electrolyte in a fuel cell undergoing poisoning, mixtures were made in such a way that the conversion of 1 mole of KOH would give us 0.5 moles of K_2CO_3 . A series of electrolyte solutions representing 0–100% conversion of KOH to K_2CO_3 were made and the steady-state current given by a fuel cell operating on each electrolyte (plus 3 ml methanol as fuel) was recorded. The cells were operated in a 100% oxygen atmosphere inside the controlled atmosphere chamber so as to prevent any further variation in the electrolyte composition with time. The steady-state current was recorded after 2000 s from the start of each cell run.

Dynamic analysis of the electrolyte was also performed to study the variation in electrolyte composition with the progress in poisoning. In the dynamic analysis of the electrolyte, a fuel cell having 1 M KOH as the electrolyte with 3 ml methanol was operated in a 70% O_2 –30% CO_2 atmosphere in the airtight chamber. An external load of 1.3 Ω was applied across the cell and the cell current was recorded using the electrochemical data recorder. The fuel cell was stopped after different time intervals and the composition of the electrolyte (concentrations of KOH and K_2CO_3) was determined. The composition of the electrolyte was determined by two methods: analyzing its conductivity and the Winkler method of volumetric hydroxide/carbonate estimation using *Bromocresol green* and *Phenolphthalein* as the

indicators [25]. Conductivity analysis was based on a calibration curve of conductivity of different mixtures of KOH and K_2CO_3 of known compositions. Conductivity was measured using a conductivity meter (CON 200, Oakton).

2.3. Electrode polarization studies

Cathodic and anodic potentiostatic polarization curves for KOH and K_2CO_3 fuel cells were obtained independently of each other. A three-electrode setup was used for polarization studies. All three electrodes were kept in one compartment. The methodology was similar for both KOH and K_2CO_3 cells. To obtain the cathodic polarization curve, open circuit potentials (OCP) of the cathode were determined. For KOH cells, it came out to be around -90 mV w.r.t. calomel electrode. The first reading was obtained by polarizing the cathode at a lower potential than the OCP i.e. at -50 mV (w.r.t. calomel) with the help of a potentiostat and the steady-state current was noted. The next reading was obtained by increasing the polarization potential by -50 mV to -100 mV. A steady-state current value was noted for this potential also. Subsequent steady-state current values were noted for every -50 mV increment and up to -350 mV to obtain the cathodic polarization curve for the KOH cell. A similar strategy was followed to obtain the anodic polarization curve.

3. Results and discussions

3.1. Accelerated testing: t_{max} and R_{max}

To elucidate the physical meaning of t_{max} and R_{max} , current versus time plots for a fuel cell running in air and in 85% O_2 –15% CO_2 is shown in Fig. 3. The plot of the fuel cell running in a carbon dioxide enriched atmosphere has a sigmoid shape, which is a characteristic of the fuel cells undergoing carbon dioxide poisoning without the replenishment of electrolyte. In the beginning, when most of the electrolyte was KOH, the current output was 83 mA. As the poisoning began

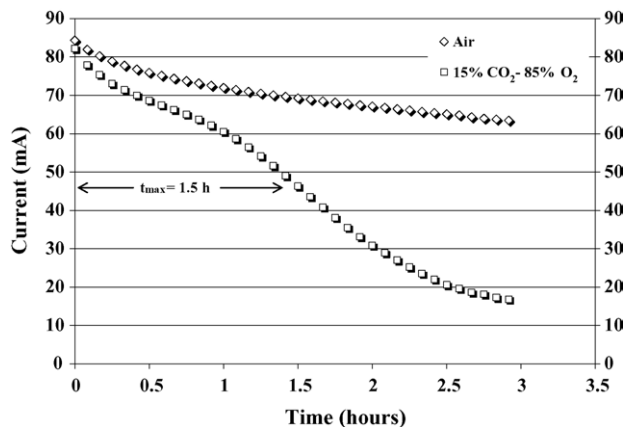


Fig. 3. Current vs. time plots for fuel cells running in air and 85% O_2 –15% CO_2 at 298 K with an applied load of 1.3Ω .

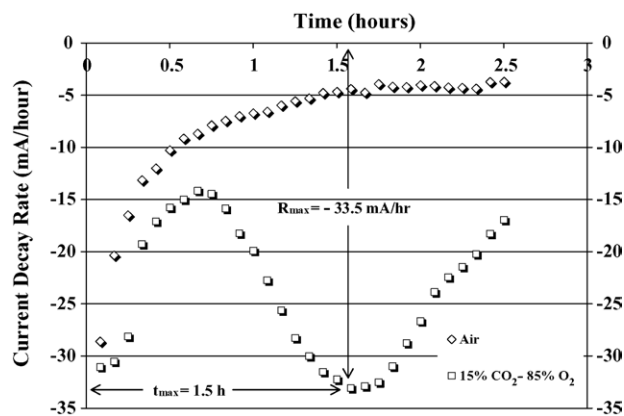


Fig. 4. Current decay rate vs. time plot for the fuel cells running in air and 85% O_2 –15% CO_2 at 298 K with an applied load of 1.3Ω .

to affect the cell, current output decreased gradually for the first hour but then started falling rapidly at around 1.5 h. At the end of the run, the current stabilized at 15 mA and remained stable no matter how long carbon dioxide enriched oxygen was fed into the fuel cell. At this time, all the KOH had been completely converted to K_2CO_3 . The time at which current decay rate was highest is referred to as t_{max} and the value of current decay rate (dI/dt) at this time is R_{max} .

These characteristic quantities are graphically represented in Fig. 4, in which rate of current decay is plotted with time. The value of the current decay rate was highest at 1.5 h (t_{max}) and had a value of 33.5 mA h^{-1} (R_{max}). Since the CO_2 “poisoning” was negligible in the fuel cell running in air (0.03% CO_2), t_{max} and R_{max} were essentially absent as shown in Fig. 4. Thus, the inverted bell shaped curve, in Fig. 4, was also a characteristic for a fuel cell being poisoned in an atmosphere enriched with CO_2 and was observed in all accelerated poisoning cell runs.

If the values of t_{max} and R_{max} are known for a fuel cell undergoing poisoning, one can precisely predict the course of the cell current with the passage of time. Therefore, we tried to find out the dependence of t_{max} and R_{max} on two independent operating parameters, i.e. atmospheric CO_2 concentration and applied load, so that just by having the knowledge of these quantities, one can predict the cell performance over a period of time in a CO_2 enriched atmosphere. In addition, the quantities t_{max} and R_{max} would also serve as benchmarks to compare the performance of a cell. Any improvement in the performance at a given atmospheric composition and load is reflected on the values of these quantities. For a given set of operating conditions, t_{max} and R_{max} have specific values but if, by some means, the process of poisoning is delayed or in other words, the cell life is prolonged, the value of t_{max} goes up and R_{max} goes down, accordingly.

3.1.1. Dependence of t_{max}

3.1.1.1. t_{max} dependence on carbon dioxide concentration.

It is logical to think that t_{max} should vary inversely with the rate of carbon dioxide poisoning. The value of t_{max} would

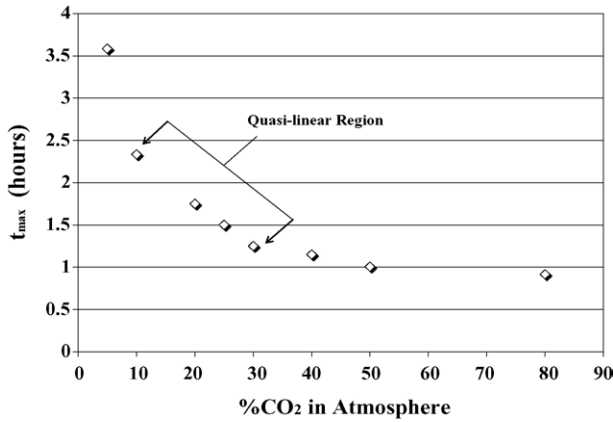


Fig. 5. Dependence of t_{\max} on the carbon dioxide concentration in the atmosphere at 298 K with an applied load of 1.3Ω .

be smaller for a faster rate of poisoning. Accordingly, as the percentage of carbon dioxide in the atmosphere increases, the value of t_{\max} decreases. Fig. 5 illustrates this concept by showing the dependence of t_{\max} on the atmospheric concentration of carbon dioxide at 298 K. The same fuel cell was operated in the controlled atmosphere chamber with different amounts of carbon dioxide and an applied load of 1.3Ω . All other experimental parameters were kept identical for all runs.

As shown in Fig. 5, t_{\max} varied quasi-linearly with the carbon dioxide concentration between 10% and 30%. As the concentration went higher than 30%, the relation lost linearity and eventually stabilized at 0.8 h. The deviation from the linearity above 30% can be explained by the fixed permeability of the carbon dioxide through the air cathode. Even though the amount of carbon dioxide in the atmosphere increased, its entry into the cell (electrolyte) was limited by the permeability of the air cathode. On the other hand, at carbon dioxide concentrations below 10%, the plot again deviated from linearity and touched the Y-axis asymptotically. The reason for the sharp increase in t_{\max} values below 10% is that, as the carbon dioxide concentration approaches zero, a fuel cell would take an infinitely long time to degrade, consequently, t_{\max} approaches infinity.

3.1.1.2. t_{\max} dependence on applied load. Interestingly, t_{\max} was also found to be a strong function of the load applied on the fuel cell. Fig. 6 shows the dependence of t_{\max} on the applied load at different concentrations of carbon dioxide in the atmosphere. As before, all experimental parameters, other than the applied load and the carbon dioxide concentration in the chamber, were kept constant.

For every CO_2 concentration, as the applied load on the cell was decreased, the value of t_{\max} went down. At 15% concentration of carbon dioxide in the atmosphere, the value of t_{\max} was 3.6 h with a load of 10.2Ω as compared to 1.5 h with a load of 1.3Ω . Small loads seemed to expedite the carbon dioxide poisoning in the fuel cells. A smaller load would withdraw a higher current from the fuel cell. It would

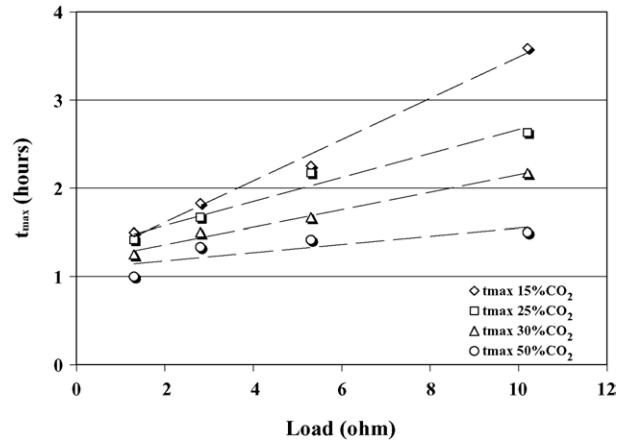


Fig. 6. Dependence of t_{\max} on the applied load at different atmospheric compositions and 298 K.

mean that the rate at which oxygen is being consumed at cathode is also high. A higher consumption rate would lead to higher uptake of oxygen from the atmosphere. Since, carbon dioxide is also present in the atmosphere, the rate of carbon dioxide uptake would go up simultaneously, leading to faster cell degradation.

Fig. 6 also shows that the dependence of t_{\max} on the applied load was linear with a positive slope. As the concentration of carbon dioxide in the atmosphere increased, the degree of dependence of t_{\max} on the applied load diminished significantly. At 15% carbon dioxide concentration, the slope of the best fit line was $0.234 \text{ h } \Omega^{-1}$, which reduced to mere $0.046 \text{ h } \Omega^{-1}$ at 50% carbon dioxide concentration. This suggests that at very high carbon dioxide concentrations ($>50\%$), the rate of poisoning would remain the same no matter what load was applied to the fuel cell. But if a fuel cell is operated in air, where carbon dioxide is negligible (0.03%), the poisoning would depend, a great deal, on the applied load.

3.1.2. Dependence of R_{\max}

3.1.2.1. R_{\max} dependence on CO_2 concentration. The dependence of R_{\max} on the concentration of carbon dioxide in the atmosphere is straight forward. Higher concentrations of carbon dioxide would lead to higher poisoning rates and, hence, larger R_{\max} values. Fig. 7 shows the variation in R_{\max} with atmospheric carbon dioxide concentration when the applied load was 1.3Ω . It is observed that R_{\max} varied quasi-linearly with carbon dioxide concentration between 5% and 30% in the atmosphere. As the concentration of carbon dioxide was increased further, the linearity was lost and R_{\max} stabilized at approximately -65 mA h^{-1} . This observation indicates that at very high concentrations of carbon dioxide ($>60\%$), R_{\max} essentially becomes constant at a specified load. The reason for this departure from linearity at high CO_2 concentrations is similar to that observed with t_{\max} in the preceding section, i.e. limited permeability of carbon dioxide through the air cathode. On the other hand, when the concentration of carbon dioxide approached zero, the R_{\max} value also

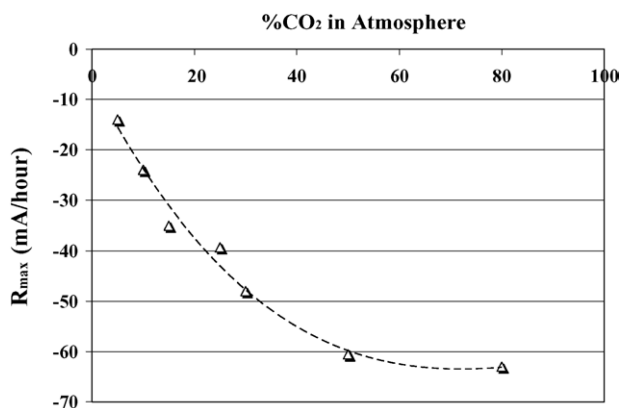


Fig. 7. Dependence of R_{\max} on the atmospheric carbon dioxide concentration at 298 K with an applied load of 1.3 Ω .

tended to zero. It can be confirmed by extrapolating the curve in Fig. 7 towards 0% concentration values. This suggests that at infinitesimally small carbon dioxide concentrations, R_{\max} would be infinitesimally small and, hence, carbon dioxide poisoning would be too negligible to measure.

3.1.2.2. R_{\max} dependence on applied load. R_{\max} was also found to be strongly influenced by the applied load, as in the case with t_{\max} . Fig. 8 shows that R_{\max} varied with the applied load in a quasi-linear fashion with a positive slope. Reasons for higher R_{\max} values at smaller loads are the same as for lower t_{\max} values at smaller loads. But unlike t_{\max} , R_{\max} became an even stronger function of the applied load at very high concentrations of carbon dioxide (>50%). Fig. 8 also indicates that as the carbon dioxide concentration was reduced, the dependence of R_{\max} on the applied load decreased and, at extremely small concentrations, this dependence would cease to exist. This is contrary to the behavior of t_{\max} , which became extremely sensitive to the applied load at lower carbon dioxide concentrations.

Therefore, we can suggest that at low carbon dioxide concentrations (<2%) the poisoning is defined by t_{\max} as R_{\max} becomes largely invariable. In the same way, at high carbon

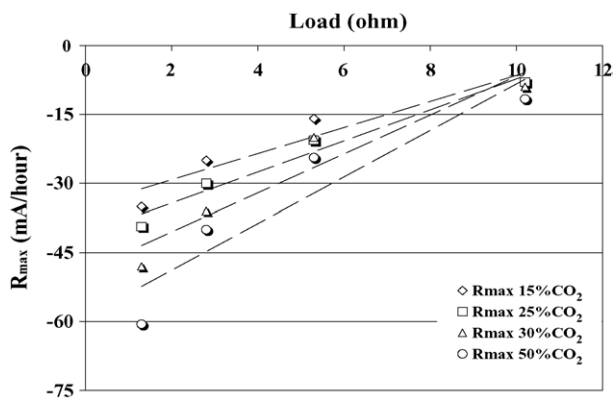
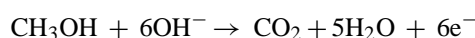


Fig. 8. Dependence of R_{\max} on the applied load at different atmospheric compositions and 298 K.

dioxide concentrations (>60%), the poisoning is defined by R_{\max} as t_{\max} becomes constant. And in intermediate concentrations of carbon dioxide, we need to specify both quantities in order to completely define the carbon dioxide poisoning in AFC. Thus, the above studies lead us to conclude that for any future testing of AFC using the accelerated poisoning methodology, the best region to study the cell is between 10% and 30% of carbon dioxide in the atmosphere.

3.1.3. CO_2 production by oxidation of methanol

One possible complication in interpreting the results could arise because of the in situ carbon dioxide production by the oxidation of the methanol. Since methanol was used as the fuel, carbon dioxide was produced as a by-product of the anodic oxidation of methanol according to the following reaction:



The above reaction shows that 1 mole of methanol produces 1 mole of carbon dioxide during complete oxidation. Thus, a passage of current would cause production of carbon dioxide at the anode and, hence, contribute to the carbon dioxide poisoning in the fuel cells. In addition, another source of carbon dioxide inside the fuel cells is the parasitic oxidation of methanol at the cathode due to methanol crossover. Therefore, it is necessary to quantify the cumulative production of carbon dioxide by the oxidation of methanol and delineate its contribution to the total carbon dioxide poisoning measured; i.e. we need to separate the contribution of the CO_2 poisoning when the CO_2 is coming through the air cathode and when the CO_2 is coming from the methanol oxidation.

By decreasing the applied load (by allowing higher current flow) we would increase the contribution of internally generated carbon dioxide (methanol oxidation) in the total carbon dioxide poisoning effect. In order to relate the K_2CO_3 resulting from the CO_2 poisoning of the electrolyte formed solely due to methanol oxidation for different applied loads, we ran our fuel cells in a 100% O_2 environment for 3.33 h. We started each run with 1 M of KOH fresh solution as the electrolyte. At the end of the experiment, the electrolyte was sampled out and its composition was determined using Winkler's method of volumetric hydroxide/carbonate estimation using bromocresol green and phenolphthalein as the indicators [25]. N_2 was bubbled for 2–3 min through the sampled electrolyte before each titration was carried out. This was done in order to get rid of any dissolved carbon dioxide in the electrolyte. Dissolved carbon dioxide might affect the titration results by forming traces of carbonic acid (H_2CO_3). Results of this composition analysis are presented in Fig. 9, which plots K_2CO_3 formed or KOH remaining as a function of the applied load after a run of 3.33 h in a 100% O_2 environment.

Fig. 9 shows that K_2CO_3 concentration resulting from the methanol oxidation decreases with an increasing applied load. As the applied load was decreased below 1 Ω , K_2CO_3 concentration rose up sharply because of a higher rate of methanol oxidation resulting from higher currents. The time

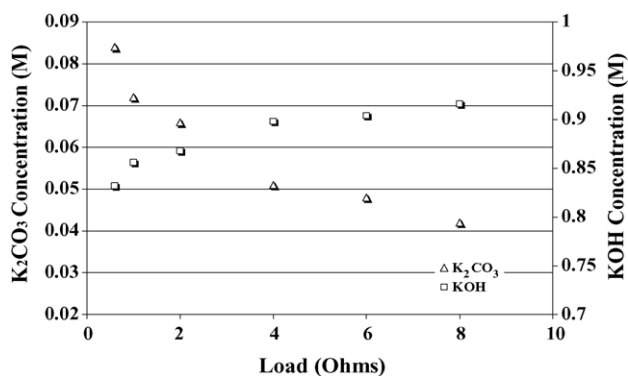


Fig. 9. Dependence of K₂CO₃ formed/KOH remaining with the applied load when a fuel cell is run for 12,000 s (3.33 h) in 100% O₂ atmosphere.

dependence of K₂CO₃ formed due to methanol oxidation at a specific applied load was also determined and is shown in Fig. 10. Fig. 10 shows a linear dependence of K₂CO₃ formed with time at an applied load of 1 Ω and an atmosphere of 100% O₂. The straight line describing this time dependence passes through the origin as shown in Fig. 10. Similar linearity in the time dependence of K₂CO₃ concentration was assumed for all the other applied loads for further calculations.

In order to determine the precise contribution of internally generated carbon dioxide in the net carbon dioxide poisoning, it was necessary to know the time at which all of the KOH converted to K₂CO₃ for any operating condition. Using the Winkler’s method of volumetric titration for the electrolyte composition analysis, it was found that at the time equal to twice of t_{max} ($t = 2 \times t_{max}$) all of KOH was converted to K₂CO₃ irrespective of the operating conditions. Thus, the amount of K₂CO₃ formed by methanol oxidation only up to $t = 2 \times t_{max}$ was needed to be determined. Since we knew the value of t_{max} for different CO₂ concentrations and applied loads, we calculated the amount of K₂CO₃ produced by internally generated carbon dioxide using the data given in Figs. 9 and 10. From Fig. 9, we determined the amount of K₂CO₃ formed at any load for 3.33 h. This value

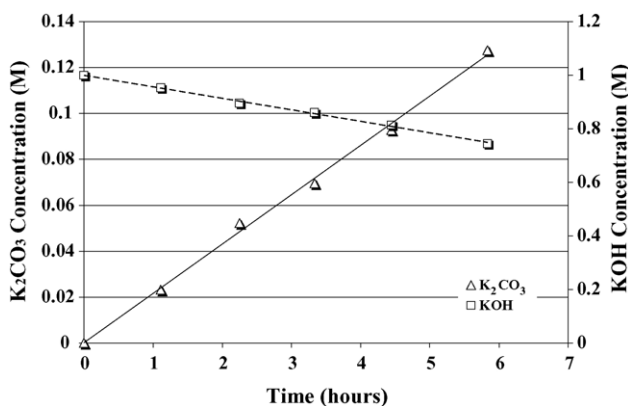


Fig. 10. Time dependence of K₂CO₃ concentration resulting from methanol oxidation at an applied load of 1 Ω and 100% O₂ atmosphere.

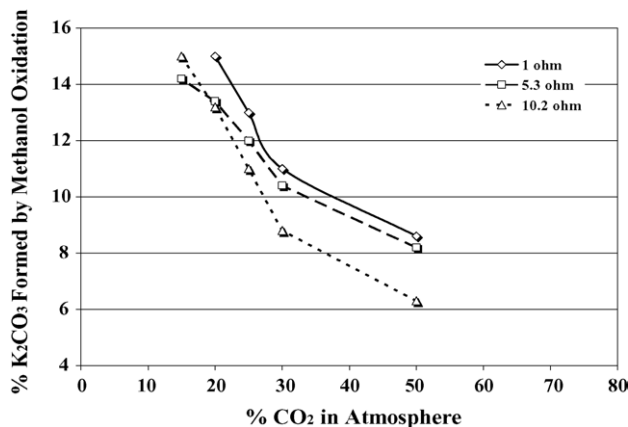


Fig. 11. Percentage of K₂CO₃ formed by internally generated CO₂ in the net K₂CO₃ produced due to total carbon dioxide poisoning.

of K₂CO₃ concentration was then scaled down using the fact that the variation of K₂CO₃ concentration with time is linear and the resulting straight line passes through the origin as shown in Fig. 10. This final value represented the fraction of K₂CO₃ formed by internally generated carbon dioxide in the total K₂CO₃ formed due to overall carbon dioxide poisoning. The results of quantification of the contribution of methanol oxidation in the net (total) CO₂ poisoning in our study are presented in Fig. 11.

We observe in Fig. 11 that the contribution of methanol oxidation in the total K₂CO₃ production decreases with the increase in carbon dioxide concentration in the atmosphere and the applied load. For the range of operating conditions in our experiments (load = 1–10 Ω and %CO₂ in atmosphere = 10–50%), the contribution of the internally generated carbon dioxide in the total carbon dioxide poisoning was determined to be between 6% and 14% depending on the CO₂ concentration and the applied load (refer Fig. 11).

3.2. Electrolyte compositional analysis

In the previous sections, we related parameters defining carbon dioxide poisoning (t_{max} and R_{max}) with the operating parameters (CO₂ concentration and applied load). The variation in a cell performance is primarily attributed to the change in the composition of its electrolyte with the progress in poisoning. In this section, the dependence of the current output of a cell on the compositional changes of its electrolyte due to carbon dioxide poisoning is elucidated. To understand the relationship between the cell current and electrolyte composition, we carried out dynamic and static analyses of the electrolyte.

3.2.1. Static electrolyte testing

In static analysis, we made precise mixtures of KOH (aq) and K₂CO₃ (aq). Using each mixture as an electrolyte, we measured the steady-state current given by a fuel cell being operated in a 100% O₂ environment. To simulate the compositional changes of the electrolyte in a fuel cell undergoing

Table 1

Composition of different mixtures in terms of KOH and K_2CO_3 concentrations and the steady-state currents obtained using the mixtures as electrolytes

Serial number	KOH molarity	K_2CO_3 molarity	Steady-state current (mA)
Mix. 1	1.0	0.00	60.0
Mix. 2	0.87	0.065	59.1
Mix. 3	0.8	0.10	58.2
Mix. 4	0.6	0.20	53.9
Mix. 5	0.5	0.25	47.6
Mix. 6	0.4	0.30	41.3
Mix. 7	0.3	0.35	35.0
Mix. 8	0.2	0.40	25.2
Mix. 9	0.1	0.45	18.1
Mix. 10	0.0	0.50	15.2

poisoning, the mixtures were made in such a way that the conversion of 1 mole of KOH would give us 0.5 moles of K_2CO_3 . The results of static analysis are tabulated in Table 1.

Fig. 12 shows the plot of steady-state current with the KOH concentration in the electrolyte. It can be seen that decreasing the KOH concentration decreases the current output of a cell, as expected. But the current did not drop appreciably until the KOH concentration was reduced from 1 M to 0.6 M. This suggests that a fuel cell undergoing poisoning would continue to give the desired current output until the KOH concentration in the electrolyte reaches a threshold value (≈ 0.6 M for our fuel cell system). This differential dependence of the cell current on the KOH concentration also explains the sigmoidal current versus time plots obtained for the fuel cells being poisoned under accelerated conditions (Fig. 3). It clearly indicates that the curves we obtained for fuel cell poisoning actually represent electrolyte compositional changes.

We called this analysis static because in each case, while measuring the steady-state current, the electrolyte composition in the vicinity of the anode and cathode was the same. This will not be true in the case of a fuel cell undergoing dynamic carbon dioxide poisoning because the majority of K_2CO_3 would be formed at the cathode, which would then diffuse to the anode through the electrolyte. Therefore, at any

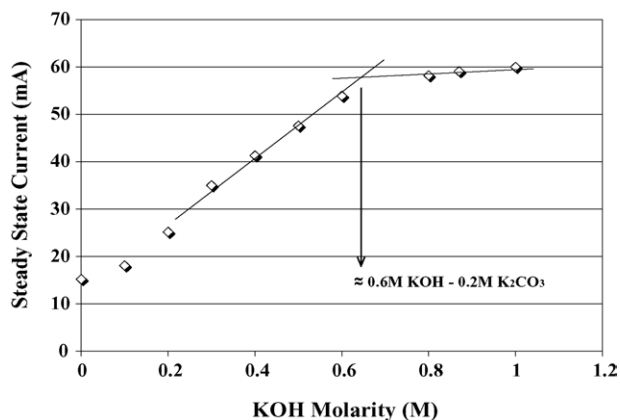


Fig. 12. Variation of steady-state current output of a fuel cell with the KOH concentration in its electrolyte.

Table 2

Composition of the electrolyte in a fuel cell, undergoing poisoning, at different time intervals and the current output at that time

Time (s)	Composition	KOH conversion rate (Mh^{-1})	Current output (mA)
250	0.87 M KOH–0.65 M K_2CO_3	1.87	59.0
500	0.78 M KOH–0.11 M K_2CO_3	1.29	54.9
1000	0.70 M KOH–0.15 M K_2CO_3	0.58	54.0
2000	0.56 M KOH–0.22 M K_2CO_3	0.50	52.5
3000	0.44 M KOH–0.28 M K_2CO_3	0.43	50.1
4500	0.28 M KOH–0.36 M K_2CO_3	0.38	46.8

time, the concentration of K_2CO_3 around the cathode would be higher than the anode. Thus, we also carried out dynamic electrolyte analysis for a better understanding of the current dependence on compositional changes of the electrolyte.

3.2.2. Dynamic testing

In dynamic analysis of the electrolyte, we started with a fuel cell having 1 M KOH as the electrolyte and operating in a 70% O_2 –30% CO_2 atmosphere with an applied load of 1.3Ω . The fuel cell was stopped at different time intervals and the composition of the electrolyte was determined. Table 2 summarizes the results of the dynamic electrolyte analysis.

Table 2 shows the conversion rate of KOH to K_2CO_3 is higher in the beginning, at a value of $1.87 Mh^{-1}$, as compared to $0.38 Mh^{-1}$ towards the end. The decrease in the conversion rate of KOH can be attributed to the limited mass transfer of the reaction product (K_2CO_3) from the reaction site (cathode) to the bulk. Current output of the cell also changed accordingly with the change in KOH concentration. Fig. 13 shows a plot of current output with KOH concentration observed in dynamic electrolyte analysis. It is compared with a similar plot, as in Fig. 12, obtained from static analysis.

A difference in the results obtained from static and dynamic analysis can be observed in this plot at lower concentrations of KOH in the electrolyte. At the same composition

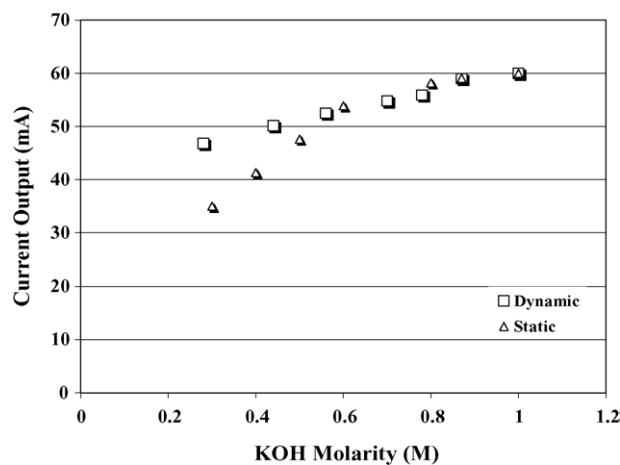


Fig. 13. Plot of current output vs. KOH concentration for static and dynamic electrolyte analysis.

of electrolyte, the current output given by a cell is higher in dynamic analysis than in static. This can be explained by the non-uniform concentration distribution of K_2CO_3 between the electrodes in a dynamically degrading fuel cell, as explained earlier. Although the overall concentration of K_2CO_3 was the same in both static and dynamic analysis, K_2CO_3 was mainly present in the vicinity of the cathode in dynamic analysis tests. Therefore, the concentration of KOH around the anode is higher in this case as compared to static analysis tests. Since it is the kinetics of methanol oxidation at the anode which is affected by K_2CO_3 concentration [1–4], the current output was found to be higher in dynamic analysis at the same electrolyte composition. This difference would diminish if the electrolyte is stirred or if the distance between the cathode and anode is reduced, which would decrease the concentration gradient of K_2CO_3 between the two electrodes.

3.3. Electrode polarization and electrolyte conductivity studies

The static and dynamic analysis of the electrolyte showed a strong dependence of current output of a fuel cell on its electrolyte composition. The conversion of KOH to K_2CO_3 by carbon dioxide poisoning makes the oxidation of fuel at the anode difficult. This conclusion is supported in the potentiostatic polarization curves of the anode and cathode for a fuel cell running on 1 M KOH and 0.5 M K_2CO_3 separately, as shown in the Fig. 14. Methanol concentration in both the cases was 2.47 M. Fig. 14 clearly suggests that the reason for low current output given by a cell in the presence of K_2CO_3 is the sluggish kinetics of methanol fuel oxidation at the anode. The kinetics of oxygen reduction at the cathode remains unchanged for both KOH and K_2CO_3 electrolytes.

Another factor which may decrease the current output of a fuel cell with K_2CO_3 as the electrolyte is the increased ohmic loss (Fig. 1) because of the lower conductivity of CO_3^{2-} ions as compared to OH^- ions [26]. Fig. 15 plots the conductivities of mixtures, tabulated in Table 1, with the KOH concentra-

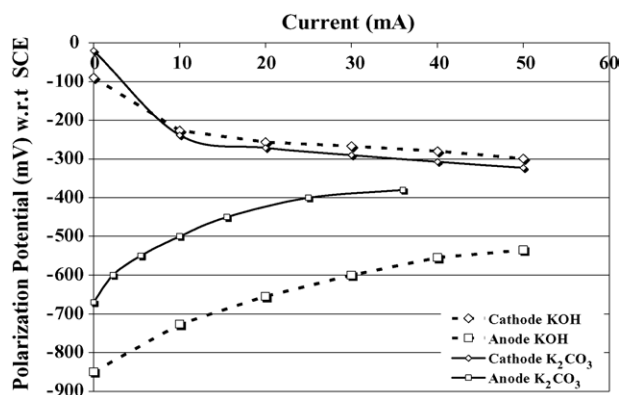


Fig. 14. Anodic and cathodic potentiostatic polarization curves of a fuel cell with pure KOH and K_2CO_3 as electrolytes. Cathodic polarization was done at potential values between cathode OCP and -300 mV. Anodic polarization was done between anode OCP and -550 mV (for KOH)/ -400 mV (for K_2CO_3) w.r.t. SCE.

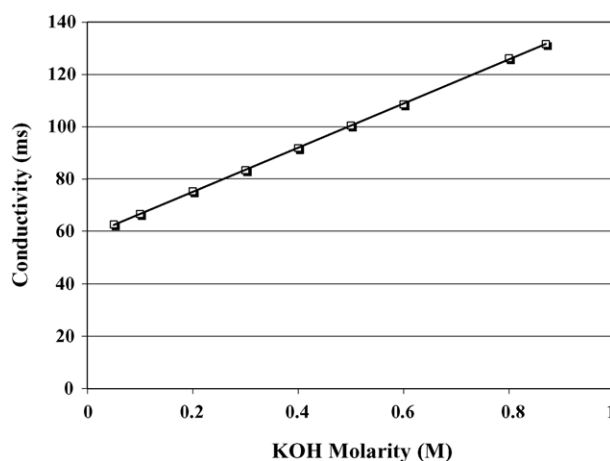


Fig. 15. Variation of electrolyte conductivity with KOH concentration.

tion in the mixtures. The dependence of the conductivity of the electrolyte on KOH concentration was found to be linear. Therefore, lesser conductivity at lower mole fractions of KOH as compared to K_2CO_3 in the electrolyte also lowers the overall performance of a fuel cell as the carbon dioxide poisoning proliferates in it.

4. Conclusion

Quantification of carbon dioxide poisoning in alkaline fuel cells is of great importance because it would enable us to predict the current output of a fuel cell running in a carbon dioxide enriched atmosphere, when the operating conditions are specified. In this study, a novel method to study and quantify the carbon dioxide poisoning in AFC, with non-circulating electrolyte, under accelerated poisoning conditions was developed. Two parameters, i.e. t_{max} and R_{max} , describing the poisoning affect under accelerated testing conditions, were defined. A lower value of t_{max} or a higher value of R_{max} would signify a higher rate of carbon dioxide poisoning. With the knowledge of these quantities, carbon dioxide poisoning can be defined, provided the other operating parameters, viz. temperature, electrolyte concentrations, etc., remain the same. Therefore, the poisoning was studied and quantified on the basis of t_{max} and R_{max} . Time at which rate of current decay is maximum (t_{max}) was found to decrease with the increase in concentration of carbon dioxide in the atmosphere and increase with the applied load. On the contrary, maximum current decay rate (R_{max}) was found to decrease with the applied load and increase with the concentration of carbon dioxide. At very low concentrations ($<2\%$) t_{max} , alone, defined the carbon dioxide poisoning as R_{max} became a constant. For the same reason, R_{max} represented the poisoning completely at high carbon dioxide concentrations ($>60\%$). Lower applied loads were found to expedite the poisoning in AFC. The reasons attributed to this are higher carbon dioxide uptake by the fuel cell and larger production of carbon dioxide by the anodic oxidation of methanol. A

detailed study of the contribution of methanol oxidation in the total carbon dioxide poisoning observed in our experiments, showed that the amount of internally generated CO₂ was about 6% to 14% of the total CO₂ (coming from the air cathode and generated internally by methanol oxidation) reacting with the electrolyte.

The effect of electrolyte composition on the current output of the AFC was also studied. It was found that a significant decrease in the cell current starts to occur only after about 60% of KOH has been converted to K₂CO₃. This yields important practical information about the time to replenish the electrolyte in AFC such that no change in power output takes place.

Also the potentiostatic polarization study of the cathode and anode in the presence of KOH (aq) and K₂CO₃ (aq) electrolytes was carried out. It indicated that the primary reason for decreases in the cell current during poisoning was sluggish methanol oxidation kinetics at the anode in the presence of carbonate. Better catalyst systems which are tolerant to carbonate as the electrolyte may, in future, allow the use of AFC in air by reducing the carbon dioxide poisoning problem.

Acknowledgements

This work was supported by NSF grant serial number 415 3767CN. The author greatly acknowledges Dr. Pat Grimes for his insightful discussions, helpful suggestions and valuable comments, and Dr. Paul Werbos and Dr. Jim Mamoh for their economical support throughout our NSF grant.

References

- [1] H. Lee, J. Shim, M. Shim, S. Kim, J. Lee, *Mater. Chem. Phys.* 45 (1996) 238–242.
- [2] S. Gamburzev, K. Petrov, A.J. Appleby, *J. Appl. Electrochem.* 32 (2002) 805–809.
- [3] E. Gülzow, *J. Power Sources* 61 (1996) 99–104.
- [4] M. Al-Saleh, S. Gultekin, A. Al-Zakri, A. Khan, *Int. J. Hydrogen Energy* 21 (1996) 657–661.
- [5] M. Schulze, E. Gülzow, G. Steinhilber, *Appl. Surf. Sci.* 179 (2001) 252–257.
- [6] J. Shim, H.K. Lee, *Mater. Chem. Phys.* 69 (2001) 72–76.
- [7] A.K. Chatterjee, R. Banerjee, M. Sharon, *J. Power Sources* 137 (2004) 216–221.
- [8] M. Schulze, E. Gülzow, *J. Power Sources* 127 (2004) 252–263.
- [9] G.F. Maclean, T. Niet, A. Prince-Richard, N. Djilali, *Int. J. Hydrogen Energy* 27 (2002) 507–526.
- [10] M. Al-Saleh, S. Gultekin, A.S. Al-Zakri, H. Celiker, *J. Appl. Electrochem.* 24 (1994) 575.
- [11] M. Al-Saleh, S. Gultekin, A.S. Al-Zakri, H. Celiker, *Int. J. Hydrogen Energy* 19 (1994) 713–718.
- [12] K.V. Kordesch, S. Gunter, *Fuel Cell and Their Application*, Wiley-VCH, Berlin, Germany, 1996.
- [13] K.V. Kordesch, in: G. Sandstede (Ed.), *From Electrocatalysis to Fuel Cells*, University of Washington Press, 1972, pp. 157–164.
- [14] E. Gülzow, M. Schulze, *J. Power Sources* 127 (1–2) (2004) 243–251.
- [15] E.H. Yu, K. Scott, R.W. Reeve, *J. Electroanal. Chem.* 547 (2003) 17–24.
- [16] E.J. Cairns, *Handbook of Fuel Cells—Fundamentals Technology and Applications*, first ed., 2003, pp. 301–309.
- [17] M. Cifrain, K.V. Kordesch, *J. Power Sources* 127 (2004) 234–242.
- [18] A.J. Appleby, F.R. Foulkes, *Fuel Cell Handbook*, Krieger Publishing Company, Malabar, FL, 1993.
- [19] V. Ahuja, R.K. Green, *Int. J. Hydrogen Energy* 21 (1996) 415–421.
- [20] V. Ahuja, R.K. Green, *Int. J. Hydrogen Energy* 23 (1998) 131–137.
- [21] E.H. Yu, K. Scott, *J. Power Sources* 137 (2004) 248–256.
- [22] E.H. Yu, K. Scott, *Electrochem. Commun.* 6 (2004) 361–365.
- [23] E. Agel, J. Bouet, J.F. Fauvarque, *J. Power Sources* 101 (2001) 267–274.
- [24] W.H. Hoge, *Air Cathodes and Materials Therefore*, US Patent 4,885,217 (1989).
- [25] D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, seventh ed., Saunders College Publishing, 1996, pp. 257–262.
- [26] P. Vanysek, in: D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press Publication, 2002, pp. 5.95–5.97.