Electrolyte management of molten-carbonate fuel cells

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Abstract

The influence of electrolyte content on the performance of molten-carbonate fuel cells is investigated Cell performance is good at a moderate electrolyte-loading ratio, but poor for both low and high ratios In the case of a low ratio, the inferior behaviour is due to an increase in IR drop through increased cell resistance and the consumption of reactant gases (through gas cross-over) With a high electrolyte-loading ratio, analysis of the electrolyte fill level in each component after cell testing reveals that poor cell performance is caused by flooding of the cathode

Introduction

The active components of molten-carbonate fuel cells (MCFCs) are composed of materials that are porous throughout Each pore is impregnated with the molten carbonate electrolyte For stable operation of a MCFC, the active area of both electrodes must be sufficient for electrochemical reaction to take place effectively at both electrodes This requires the formation of a three-phase interface of gas–electrolyte–electrode When the electrolyte fill level in the electrodes is too low, the active area required for adequate electrochemical reaction cannot be achieved On the other hand, the rapid diffusion of reactant gases to the reaction site is disturbed in the case of an extremely high electrolyte fill level Thus, the fill level in both electrodes must be optimized

The electrolyte loading must allow good ionic conduction and must prevent gas cross-over through the matrix Restricted ionic conduction would cause high cell resistance, and, consequently, lowering of the cell performance through an increase in the ohmic (IR) drop Gas cross-over through the matrix would give rise to a decrease in the reactant gases and thereby reduce the cell performance

In this study, the cell performance and electrolyte fill level in each component have been investigated by varying the electrolyte-loading ratio

Experimental

Single cells were assembled with an electrolyte-loading ratio of 100, 130, 160, 200, 230, 250, 260 or 290% A 100% ratio was defined as giving sufficient electrolyte to fill the void volume of the matrix

The cell construction is shown in Fig 1 The active area of the electrodes was 25 cm^2 The anode was fabricated from Ni–3wt %Al alloy powder The latter was mixed with organic materials (binder, plasticizer, etc) and solvents in a ball-mill The resulting slurry was tape-cast and a green tape was obtained by drying off the solvents The green tape was sintered at ~1000 °C in a reductive atmosphere after burning out the organics The anode obtained by this procedure had a porosity of ~50% and a thickness of ~0 75 mm The mean pore-size was ~5 μm The nickel plaque for the cathode was fabricated by sintering Inco 287 Ni powder at 700 to 800 °C in a N$_2$ atmosphere The porosity and thickness of the plaque were ~75% and ~0 75 mm, respectively The mean pore-size was ~10 μm The Ni plaque was oxidized to NiO during cell heat-up to 650 °C The matrix was composed of LiAlO$_2$ and a green tape was fabricated using the method described above for the anode The organics in this green tape were burned out to produce a LiAlO$_2$ porous material during the cell heat-up procedure The porosity, thickness and mean pore-size of the resulting matrix were ~50%, ~0 50 mm and ~0 1 μm, respectively

Pore-size distributions of the above cell components are presented in Fig 2 The data include the distribution for the cathode both before and after oxidation in the cell It can seen that the cathode has a bimodal structure after oxidation

The active components were assembled into a cell with Ni and S S 316L perforated current-collectors and S S 316L cell frames The latter were ribbed to allow the flow of reactant gases
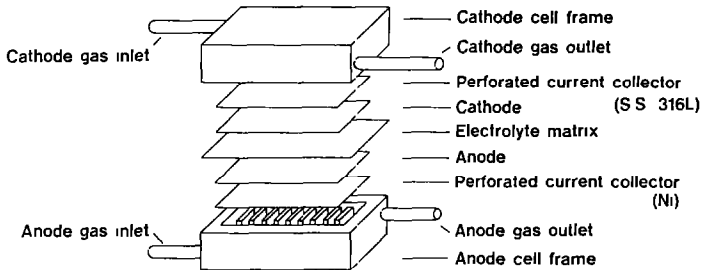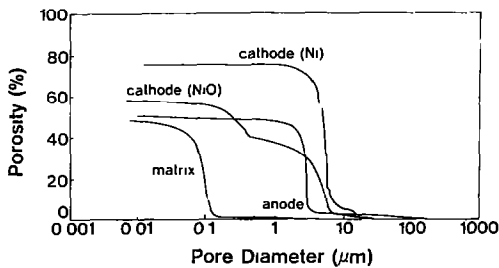

Fig 1 Cell construction

Fig 2 Pore-size distributions in MCFC active components

The electrolyte was a 62 to 38 mol % Li_2CO_3–K_2CO_3 mixture and was loaded in single cells to levels between 100 and 290% The pores of each component became impregnated with electrolyte during cell heat-up

The cell performance (polarization characteristics and dependence of cell voltage on gas utilization) was measured upon stabilization, this was usually after ~50 h of cell service at 650 °C The anode gas was 80% H_2–20% CO_2 (45 °C humidified) and the cathode gas 70% air–30% CO_2 Cell resistance and N_2 gas cross-over were monitored in the anode gas outlet Cells with 200, 250 and 290% ratios were operated for 1000 h in order to study the durability of the system

The cells were disassembled after testing, and the electrolyte fill level in each active component was examined by extracting the carbonate electrolyte with a mixed solution of 70% acetic acid and 30% acetic anhydride The fill level was determined by the difference in weight before and after the electrolyte extraction

Results and discussion

Electrolyte distribution

The electrolyte fill level in each component after three days of cell testing is given in Fig 3 The results show that the fill level of each component increased as the electrolyte-loading ratio was increased The electrolyte fills the pores of the matrix to a greater extent than the electrodes This is because the matrix has the smallest pore size The electrolyte fill level in the matrix was ~80% when the loading ratio was below 130%

The fill level in the cathode increases almost linearly as the electrolyte loading ratio increases By contrast, the level in the anode exhibits a constant value at ~10% up to a loading ratio of 200%, and then increases Electrolyte goes more readily into the cathode than the anode because the former electrode is composed of oxide (as opposed to metal) and is therefore more amenable to electrolyte wetting
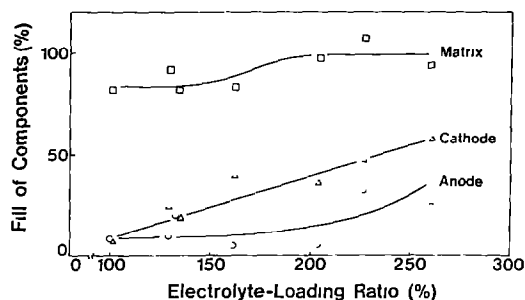

Fig 3 Electrolyte distribution in active components (O) anode, (△) cathode, (□) matrix

Polarization characteristics

Figure 4 gives the relationship between cell performance and electrolyte-loading ratio. A good stable performance was obtained for a ratio between 160% and 260%. The open-circuit voltage (*OCV*) and cell voltage at 150 mA cm^{-2} were 1 07 V and 0 90 to 0 92 V, respectively. On the other hand, when the cell was tested with a ratio of 100%, the cell performance was found to be extremely low. Although better than at a 100% ratio, the performance was still inferior at 130 and 290%. For example, for a 130% ratio, the *OCV* was 1 04 V (i e, below the theoretical value 1 08 V, under the existing experimental conditions [1]) and the cell voltage at 150 mA cm^{-2} was 0 87 V. Compared with the stable values (see above), it is interesting to note that the cell voltage exhibited a greater decrease than the *OCV*. This tendency was more marked when the cell was tested at a 100% ratio. The cell voltage at open circuit and at 150 mA cm^{-2} was 0 98 and 0.1 V, respectively.

At a 290% ratio, the *OCV* was 1 07 V, but the cell voltage at 150 mA cm^{-2} was 0 86 V, a value that was somewhat lower than that obtained between the 0 and 260% loading ratios.

Cell resistance and gas cross-over

Not only cell resistance but also N_2 gas cross-over increased on lowering the electrolyte-loading ratio (see Fig 5). The behaviour was particularly marked at ratios below 130%. This appeared to result from an increase in *IR* drop, increased cell resistance, and the consumption of reactant gases by cross-over through the matrix. The fill level of the matrix was about 80% (Fig 3). Sufficient electrolyte to maintain adequate ionic conduction and prevent gas cross-over through the matrix could not be achieved in this range. The minimum loading ratio of electrolyte for satisfactory and stable MCFC performance was determined to be > 160%.

Gas utilization characteristics

Dependence of cell voltage at 150 mA cm^{-2} on cathode gas utilization (U_{ox}) is shown in Fig 6. The cell tested at an electrolyte loading ratio of 200% showed stable performance until 70% oxidant utilization, but the cell
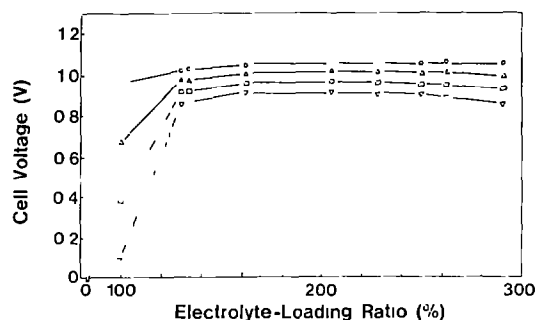

Fig 4 Influence of electrolyte loading ratio on MCFC performance (O) OCV, (△) 50 mA cm^{-2}, (□) 100 mA cm^{-2}, (▽) 150 mA cm^{-2} U_f 14%, U_{ox} 13%
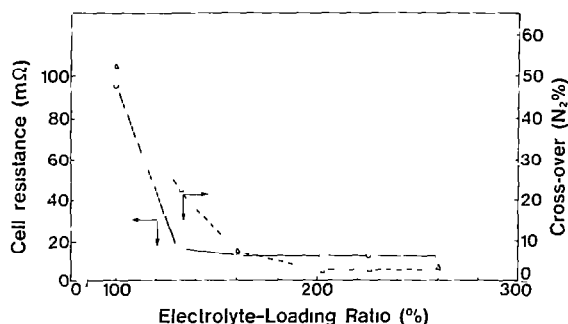
Fig 5 Influence of electrolyte-loading ratio on (O) cell resistance (△) gas cross-over U_1 40%, U_{ox} 40% Current density = 150 mA cm^{-2}
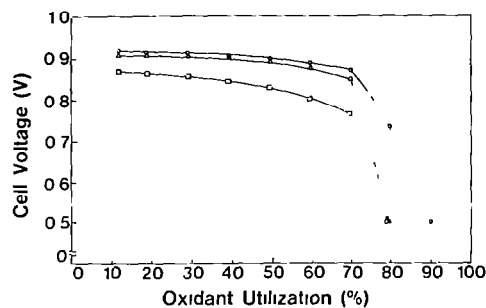

Fig 6 Dependence of cell voltage on oxidant utilization Electrolyte-loading ratio (O) 200%, (△) 260%, (□) 290% U_1 14% Current density 150 mA cm^{-2}

voltage declined rapidly at 80% utilization The cell voltage became unstable at 90% utilization and dropped below 500 mV By contrast, the voltage of the cell tested at a 260% loading ratio gradually declined from 60% utilization and became unstable and dropped below 500 mV at 80% utilization

The voltage of the cell with a 290% loading ratio was lower than the cells mentioned above The decay was greater because of the hindrance to the diffusion of the cathode gas caused by the high electrolyte fill level in the cathode [2, 3]

The dependence of cell voltage at 150 mA cm^{-2} on anode gas utilization (U_f) is shown in Fig 7 The behaviour is similar at loading ratios of 200 and 260% The voltage of the cell with a 290% ratio, however, is lower, but the subsequent decline is less This appears to be due to fast diffusion of the anode gas

Life performance

The life performance of cells with 200, 250 and 290% electrolyte-loading ratios is shown in Fig 8 The best initial results were obtained with the lowest ratio But cells with higher ratios yielded better life performance For ratios of 250 and 290%, the cell voltages after 1000 h of life were higher
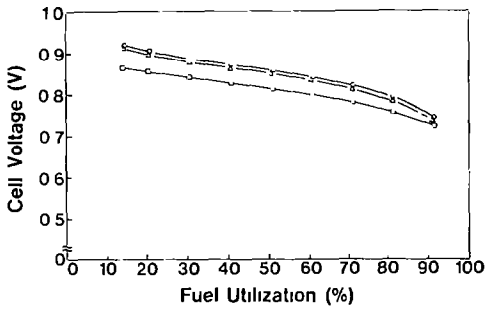
Fig 7 Dependence of cell voltage on fuel utilization Electrolyte loading ratio (O) 200%, (△) 260%, (□) 290% U_{ox} 13% Current density 150 mA cm^{-2}
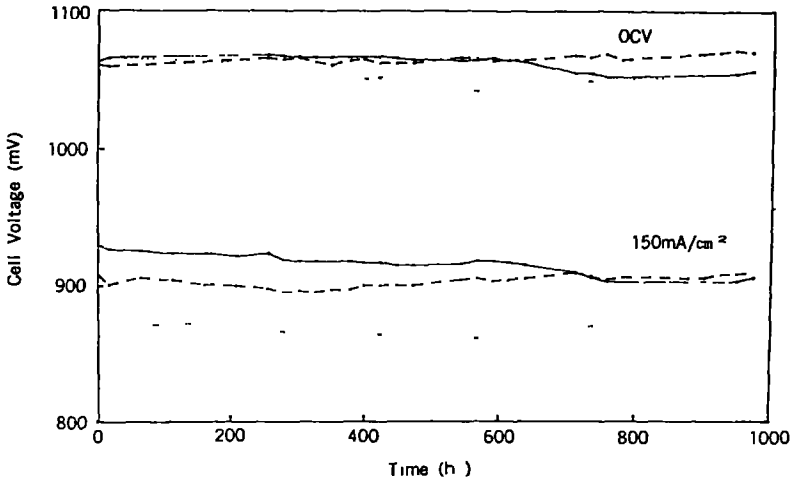

Fig 8 Cell performance history Electrolyte loading ratio (——) 200%, (- - - -) 250%, (   ) 290% U_f 14%, U_{ox} 13% Current density = 150 mA cm^{-2}

TABLE 1

Summary of MCFC life performance

Electrolyte-loading ratio (%)	Initial voltage[a] (mV)	Voltage[a] after 1000 h (mV)	Decay rate (mV/1000 h)
200	920	905	−15
250	900	905	+5
290	860	880	+20

[a] At 150 mA cm^{-2}

than those recorded initially The life performances and accompanying decay rates are summarized in Table 1

In the case of a high electrolyte-loading ratio, the excess electrolyte decreased to a moderate level with time Thus, the cell performance after
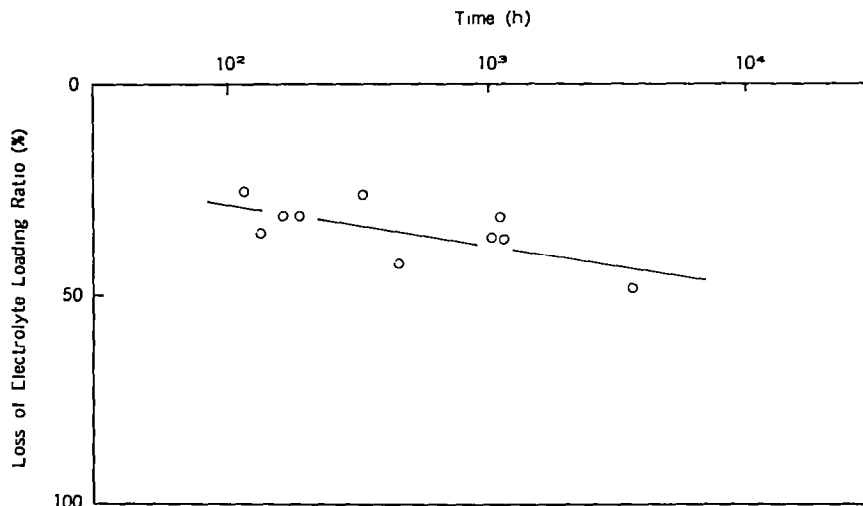
Time (h)

Fig 9   Loss of electrolyte-loading ratio

1000 h appeared to become higher than the initial performance The loss of electrolyte-loading ratio is plotted against cell operating time in Fig 9 From least-squares analysis, it is concluded that loss of electrolyte-loading ratio (%) = $10\,0\,\log t + 8\,1$ where t is in h The loss in the ratio is ~40% after 1000 h On this basis, a high electrolyte-loading ratio, such as 290%, is necessary for long cell life

Conclusions

The influence of electrolyte-loading ratio on the performance of molten-carbonate fuel cells has been investigated

The minimum electrolyte-loading ratio for good and stable performance is > 160% At ratios below 130% there was an increase both in IR drop and reactant gas cross-over These effects caused a deterioration in cell performance By contrast, an electrolyte-loading ratio > 290% was excessive and resulted in flooding of the cathode The latter impeded the diffusion of gas to the electrochemical reaction sites Nevertheless, a high electrolyte-loading ratio of 290% is advantageous in respect to providing long cell life

References

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