ANL-79-55

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

CRITICAL SURVEY ON ELECTRODE AGING
IN MOLTEN CARBONATE FUEL CELLS

by

K. Kinoshita*

Chemical Engineering Division

December 1979

*Now at SRI International, Menlo Park, California

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. EXPERIMENTAL STUDIES ON ELECTRODES FOR MOLTEN CARBONATE FUEL CELLS	2
A. Electrode Materials	2
1. Iron	2
2. Silver	8
3. Copper	8
4. Cobalt	9
5. Nickel	9
6. Noble Metals	10
7. Alloys Containing Nickel	10
B. Electrode Structures	11
III. AGING AND DEGRADATION OF MOLTEN CARBONATE FUEL CELL ELECTRODES .	15
A. Corrosion of Electrode Materials	15
1. Thermodynamic Considerations	15
2. Experimental Studies	20
3. Effect of Electrolyte Composition	25
B. Sintering of Porous Electrodes	25
1. Sintering Mechanisms	26
2. Experimental Studies on Electrode Sintering	30
3. Inhibition of Sintering in Fuel Cell Electrodes	40
C. Poisoning and Contamination of Electrodes	47
1. Sulfur	47
2. Chloride	49
IV. CONCLUDING REMARKS AND RECOMMENDATIONS	50
ACKNOWLEDGMENT	53
REFERENCES	53

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Potential <i>vs</i> $p\text{CO}_2$ for the System Nickel-Ternary Carbonate Eutectic at 873 K	17
2.	Potential <i>vs</i> $p\text{CO}_2$ for the System Iron-Ternary Carbonate Eutectic at 873 K	18
3.	Potential <i>vs</i> $p\text{CO}_2$ for the System Silver-Ternary Carbonate Eutectic at 873 K	18
4.	Potential <i>vs</i> $p\text{CO}_2$ for the System Gold-Ternary Carbonate Eutectic at 873 K	19
5.	Potential <i>vs</i> $p\text{CO}_2$ for the System Platinum-Ternary Carbonate Eutectic at 873 K	19
6.	Improvements in Endurance of Molten Carbonate Cells with Stabilized Anode Structures Reported in 1975 by King	26
7.	Performance of Cell DOE-2 with a Ni Anode	31
8.	Performance of Cell 7-17 with a Ni Anode	32
9.	Change in Porosity of Ni Electrodes with Sintering at 973 K in Low BTU Fuel	33
10.	Surface Area Change of Gould Sintered Ni Electrode at 973 K in Low BTU Fuel	34
11.	Intermediate Stage Sintering Behavior of Gould Sintered Ni Electrode at 973 K in Low BTU Fuel	35
12.	Performance of Cell DOE-10 with a Co Anode	36
13.	Densification Rates of Cu and Ni Heated at 1273 K in H_2	37
14.	Surface Area <i>vs</i> Concentration of Lithium Additions in NiO Powders	39
15.	Performance of Cell with a Proprietary Anode	40
16.	Mercury Porosimetry Analysis for Relative Mean Pore Size of Proprietary Anodes after Test in Molten Carbonate Fuel Cells .	41
17.	Performance of Cell DOE-5 with a Co-10% Cr Anode	44
18.	Normalized Amplitude Decay for Surface, Profile on 99.999 Ni Crystals at 1023 K in Tank Hydrogen	46

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Description of Molten Carbonate Fuel Cells	3
2.	Characteristics of Electrodes for Molten Carbonate Fuel Cells . .	12
3.	Standard Electrode Potentials at 925 K	22
4.	Structural Analysis of Ni Anodes Tested in Molten Carbonate Fuel Cells at 923 K	33
5.	The Physical Properties of Porous Electrodes Heated at 923 K in Low BTU Fuel	34
6.	Stabilized Anode Structures For Molten Carbonate Fuel Cells . . .	42
7.	Characterization of Nickel and Nickel-Cobalt Anodes after Operation in Molten Carbonate Fuel Cells at 925 K	43
8.	Sulfidation Reactions and Log P_{H_2}/P_{H_2S} Just Before Sulfide Formation Occurs with Various Metals at 923 K	48

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ABSTRACT

To evaluate potential electrodes for molten carbonate fuel cells, we reviewed the literature pertaining to these cells and interviewed investigators working in fuel cell technology. In this critical survey, the effect of three electrode aging processes--corrosion or oxidation, sintering, and poisoning--on these potential fuel-cell electrodes is presented. It is concluded that anodes of stabilized nickel and cathodes of lithium-doped NiO are the most promising electrode materials for molten carbonate fuel cells, but that further research and development of these electrodes are needed. In particular, the effect of contaminants such as H₂S and HCl on the nickel anode must be investigated, and methods to improve the physical strength and to increase the conductivity of NiO cathodes must be explored. Recommendations are given on areas of applied electrode research that should accelerate the commercialization of the molten carbonate fuel cell.

I. INTRODUCTION

After the classic study of Broers¹ in the late 1950's, numerous research groups in the United States and Europe pursued the development of molten carbonate fuel cells. However, this flurry of research and development activity diminished in the late 1960's, and only recently, through the efforts of the programs sponsored by the Department of Energy (DOE), Electric Power Research Institute (EPRI), and industry has interest in molten carbonate fuel cells been renewed. To aid in advancing the molten carbonate fuel cell to commercialization, representatives of government and industry proposed that a critical survey of the fuel cell technology be undertaken. Therefore, we are undertaking a critical survey of the literature on the aging and degradation of electrodes in molten carbonate fuel cells. This survey, which includes personal contacts with investigators in fuel cell technology, will serve as the basis for defining possible needs for applied research in such areas as electrode sintering, electrode corrosion or chemical oxidation, and electrode poisoning or contamination. The aim is to identify areas in which technical information is needed to accelerate the commercialization of molten carbonate fuel cell technology.

This report is divided into three sections. The first section is a review of the published literature on the structure, composition, and aging of electrodes used in molten carbonate fuel cells tested prior to the inception of the program funded by DOE in about 1976. The second section discusses in more detail the more recent experimental data on the aging

and degradation of electrode materials in molten carbonate fuel cells. The third section summarizes the state-of-the-technology of electrodes used in molten carbonate fuel cells and presents recommendations for research required to overcome electrode aging problems, which are based on evaluation of published experimental data and discussions with investigators in the fuel cell community.

II. EXPERIMENTAL STUDIES ON ELECTRODES FOR MOLTEN CARBONATE FUEL CELLS

The evolution of the molten carbonate fuel cell from the early part of the 1900's to the 1950's has been discussed in several publications.^{1,2-4} In particular, significant contributions made by Baur *et al.*⁵ and Davtyan⁶ eventually led to the development of the molten carbonate fuel cell in the late 1950's by Broers.¹ In the mid 1970's, Ackerman⁷ reviewed the state of technology for the electrodes used in molten carbonate fuel cell and discovered that the anode is generally a porous Ni structure (0.5-mm thick, 60% to 70% porosity, and $\sim 5 \mu\text{m}$ mean pore size) stabilized against sintering by using additives and that the cathode is generally a porous structure of NiO constructed by *in situ* oxidation of sintered Ni structures (0.3-mm thick, 70 to 80% porosity, and $\sim 10 \mu\text{m}$ mean pore size). Also in the mid 1970's, the Institute of Gas Technology (IGT) reviewed the development of the molten carbonate fuel.⁸ Using this review and a further review of the literature, we were able to compile a list of the major components and operating temperature of fuel cells under development from 1921 to 1975 (Table 1). In this table, attention is focused on the electrode materials used in molten carbonate fuel cells containing an electrolyte mixture of Li_2CO_3 , Na_2CO_3 , and K_2CO_3 ; these cells were operated at 673 to 1023 K with a variety of fuel and oxidant gases. The molten carbonate electrolyte was generally contained in a metal oxide ceramic matrix, although several investigators operated cells with "free electrolyte."

A. Electrode Materials

In Table 1, the major electrode materials are iron, silver, copper, cobalt, nickel, noble metals (*e.g.*, Au, Pt, and Pd-Ag), and alloys containing nickel. Results on the aging and degradation of these electrode materials are discussed below.

1. Iron

The electrodes used by Baur *et al.*⁵ consisted of iron wire clippings for the anode and magnetite (Fe_3O_4) granules for the cathode; both materials were placed inside circular holes drilled into long blocks of porous MgO which served as electrode containers. Subsequent to the electrode design of Baur *et al.*, Davtyan⁶ used anodes consisting of a paste mixture of Fe powder, Fe_2O_3 , and clay, and cathodes consisting of a mixture of Fe_3O_4 , Fe_2O_3 and clay. However, the cells of Baur *et al.* and Davtyan gave poor performance due to electrode instability. Broers^{1,4} reported that Fe_3O_4 in the cathode was oxidized within 24 hours to Fe_2O_3 and that the electronic conductivity of this electrode was reduced enough to make the electrode useless. His studies¹ also showed that Fe_3O_4 in the anode was reduced to Fe and that the accompanying volume change caused cracks in the electrolyte

Table 1. Description of Molten Carbonate Fuel Cells

Anode	Cathode	Alkali Species in Carbonate Melt	Electrolyte Support	Temperature, K	Fuel	Oxidant	Reference
Ag	Ag	Na, K	MgO	993	Town gas	Air	1
Fe	Ag	Li, Na, K	MgO	993-1003	Town gas N ₂ /CO ₂	O ₂ Air	
316 SS	316 SS	Li, Na	MgO	837-1123	H ₂ /H ₂ O	Air	3
Ni gauze	Ni				CO/CO ₂	Air/CO ₂	
Ag gauze	Ni (lithiated)						
Ni	Ag gauze						
MnO ₂ (lithiated)	Iron oxides						
316 SS activated with Fe-Fe oxide							
Pt	Ag	Li, Na	MgO	773-973	H ₂ CO CH ₄ CO/CO ₂	O ₂ /CO ₂	5
Ni		Li, Na, K					
Fe, Fe-Ni							
Co							
Cu							
Cr							
Mn							
Ag							
Fe-Mgo	Fe ₃ O ₃ -MgO	Na, K	MgO	~1100	H ₂	Air	6
Fe ₂ O ₃ -Fe-clay	Fe ₂ O ₃ -Fe ₃ O ₄ -clay	Na + other oxides of Co, Ce, P, Sn, Th, W	Sand, monazite clay, quartz	973	H ₂ /CO	Air	7
Ni	Ag	Li, Na, K	MgO	873-973	CO ₂ /CO/H ₂	Air/CO ₂	9
Fe							
Cr-Ni-Fe							
Ag							
Inconel							

(Cont'd)

Table 1. (Cont'd)

Anode	Cathode	Alkali Species in Carbonate Melt	Electrolyte Support	Temperature, K	Fuel	Oxidant	Reference
Ni Fe Nichrome Cu	Ag	Li, Na, K	MgO	973-1003	CH ₄ /H ₂ O CO ₂ /CO/H ₂	Air/CO ₂	10
Ag-ZnO Fe-Ni-Cu Flaked Ni Fe Ni	Ag	Li, Na Li, Na, K	MgO	933-1003	CO/CO ₂ CH ₄ /H ₂ O H ₂ /CO ₂ CH ₃ OH/CO ₂ CH ₄ /CO ₂	O ₂ /CO ₂ /N ₂	11
Ag-ZnO	Ag-Zn	Li, Na	MgO	823-973	H ₂ CO CH ₄ CH ₃ OH Kerosene C ₃ H ₈ /H ₂ O	Air	12, 13
Ag	Ag	Li, Na	MgO	923	H ₂ /CO/CO ₂ /N ₂ /H ₂ O	Air/CO ₂	14
Ag	Ag	Li, Na	MgO	873	H ₂ H ₂ /CO ₂	Air/CO ₂	15
Ni Pt Cu Ag	Ag	a	a	673-773	H ₂ CH ₄	a	16
Ag	Ag Nichrome	Li, Na, K	MgO Al ₂ O ₃ ZrO ₂	973	H ₂	Air/CO ₂	17

(Cont'd)

Table 1. (Cont'd)

Anode	Cathode	Alkali Species in Carbonate Melt	Electrolyte Support	Temperature, K	Fuel	Oxidant	Reference
Ni Graphite-Ni Ag	Ag/ZnO	Li, Na	MgO	873	H ₂ /CO ₂	Air/CO ₂	18
Ag-Ni	Ag-Ni	a	MgO	873	H ₂	Air	19
Ni Inconel	Ag	Li, Na, K	None	775-923	C ₃ H ₈	Air	20
Ni 431 SS	Ag Ni Au	Li, Na, K	None	773-923	H ₂	O ₂	21
Ni	Ag	Li, Na, K	MgO	853	Reformed CH ₄	O ₂ /CO ₂	22
Ni	Ag	Li, Na	MgO	923-1023	CH ₄ /CO	O ₂ /CO ₂ /He	23
Pg-Ag foil	Ag paint	Li, Na	MgO	873	Reformed CH ₄	Air/CO ₂	24
Inexpensive metals	Ag	Li, Na	MgO	873	H ₂	Air/CO ₂	25
Pd Alloy film-Pt	Ag	Li, Na, K	MgO	873	H ₂	O ₂ /CO ₂	26
Co Ni Pt	Ag	Li, Na	MgO	823-1023	H ₂ CO CH ₄ C ₃ H ₈	O ₂ /CO ₂	27
Ni	Ag-plated SS	Li, Na	MgO	893	H ₂ /CO ₂ /N ₂	Air/CO ₂	28
Ni	CuO-Cu Ag	Li, Na, K	MgO	973	H ₂ /CO ₂	Air/CO ₂	29, 30

(Cont'd)

Table 1. (Cont'd)

Anode	Cathode	Alkali Species in Carbonate Melt	Electrolyte Support	Temperature, K	Fuel	Oxidant	Reference
Ni	Ag-Cu ₂ O-ZnO	Li, Na	MgO	823-923	H ₂ CH ₄ /H ₂ O	Air/CO ₂	31
Graphite-Pd	Ag	a	MgO Stabilized Al ₂ O ₃	873	H ₂	Air/CO ₂	32
Ni	Ag-plated SS	Li, Na	MgO	873-923	H ₂ /H ₂ O/CO ₂	Air/CO ₂	33
Ag-Pd foil	Ag NS30 SS Li ₂ O-doped NiO Li ₂ O + Na ₂ O-doped NiO	Li, Na, K	none	833-873	H ₂ /CO ₂	O ₂ O ₂ /CO ₂ O ₂ /H ₂ O	34
a	Ag	Li, Na, K	a	953	a	O ₂ /CO ₂	35
Ni	Ag	Li, Na, K	MgO	803-1053	H ₂ /CO ₂	O ₂ /CO ₂ /N ₂	36
Ni	Ag	a	a	977	Reformed CH ₄	O ₂ /CO ₂	37
Ni	Ag-plated SS	Li, Na, K	a	973	Reformed hydrocarbons	O ₂ /CO ₂	38
Ni	NiO	Li, Na	MgO	873-913	H ₂ /H ₂ O H ₂ H ₂ O/CO CO	O ₂ /CO ₂	39
Ni-Pt	Ag				H ₂ /CO/H ₂ O H ₂ /CO ₂ CO/CO ₂		
Ni-Pd	Cu						
Ni	Ag-CuO	Li, Na	MgO LiAlO ₂	923	Reformed CH ₄	Air/CO ₂	40
Ni	Ag	Li, Na, K	Rare metal oxides	773-873	H ₂ CO C ₃ H ₈	O ₂ /CO ₂	41

(Cont'd)

Table 1. (Cont'd)

Anode	Cathode	Alkali Species in Carbonate Melt	Electrolyte Support	Temperature, K	Fuel	Oxidant	Reference
Pd	Ag	Li, Na, K	a	813-923	CH ₄ C ₂ H ₄ C ₂ H ₆ C ₃ H ₈	O ₂ /CO ₂	42
Ni	Ag	Li, Na	LiAlO ₂	1023	H ₂ /CO ₂	Air/CO ₂	43
Ni fiber	Cu fiber Ni fiber Ag paint	Li, Na, K	MgO	973	H ₂ /CO/CO ₂ /CH ₄	Air/CO ₂	46
Ni	Au	Li, Na, K	a	973	a	a	49
Pt	Nichrome	Li, Na, K	MgO	773-973	H ₂	O ₂ /CO ₂	50
Ni	NiO	a	a	923	H ₂ -rich gas	O ₂ /CO ₂	51
Ag	Ag	Li, Na, K	MgO	883	H ₂ CH ₃ OH C ₃ H ₈ CO CH ₄	O ₂ /CO ₂	52
Ni Pd Pt	Ag	a	MgO	773-973	H ₂ CO Hydrocarbons	O ₂ /CO ₂	53

^aComposition was not specified in publication.

tubes or discs, thereby destroying the cells within a few days. Furthermore, Broers^{9,10} pointed out that Fe and Cr-Ni-Fe anodes must be operated near their reversible potential, otherwise these electrodes oxidize in the molten carbonate. Broers and Schenke¹¹ tested anodes of Fe-Ni-Cu (powder mixture containing equal weight percent of each element) in a cell at 1003 K. Their results suggest that the metal electrode is gradually oxidized during cell operation. Besides the above mentioned papers, the only other published results describing the use of iron containing electrodes in molten carbonate fuel cells were found in the work of Gorin and Recht². They reported that porous stainless steel activated with mixtures of iron and iron oxide showed good performance as an anode with CO-CO₂ fuel gas. Ferric oxide was also tried as a cathode material, but was found to react with Na₂CO₃ to form NaFeO₂.

2. Silver

Silver has been used extensively as both an anode^{1,2,4,9,11-17,52} and a cathode^{1,2,4,9,15,11-13,46,52,53} material in molten carbonate fuel cells. Broers^{1,4,11} reported that Ag is an "ideal oxygen electrode" in cells operating at 773 K or greater with an oxidant gas containing O₂ and CO₂. Silver powder used as a porous cathode was found to be virtually non-polarized at current densities of up to 150 mA/cm² at 773 K. However, Broers *et al.*¹⁰ observed that the potential of an Ag cathode was unstable when operated at current densities of 125 mA/cm² at 973 K in an air/CO₂ mixture; the reason for this unstable potential was not discussed. On the basis of short term studies (<1000 h), other experimenters^{4,12,13,24,25} also reported that Ag cathodes have very little polarization; and, therefore, they suggested that Ag is a suitable cathode for molten carbonate fuel cells. However, a wealth of information is available that indicates Ag is not suitable as a cathode for long-term application (>1000 h). For example numerous studies^{21,32,34} have shown that Ag corrodes in molten carbonate electrolytes at cell operating temperatures, (these observations will be discussed in more detail). Silver does not appear to be an effective anode in a fuel cell with CO₂/H₂ (50/50 vol %) gas mixtures, according to Broers⁹.

Very little information was found in the literature concerning the effect of sintering on the stability of porous Ag electrodes in molten carbonate fuel cell environments. Trachtenberg³³ performed a post-test examination of a fuel cell that had operated for approximately 800 h at 873 K and found evidence of sintering in the Ag cathodes and a decrease in surface area of the Ag particles. Salvadori *et al.*⁴⁰ reported that when CuO is added to porous Ag cathodes, rapid sintering is prevented because the additive limits the intergranular diffusion of Ag. Chambers and Tantram^{12,13} used electrodes consisting of porous layers of silverized ZnO (0.05-cm thickness) in their fuel cells, which operated for 1000 h with no deterioration in performance. According to Tseung^{18,44} ZnO inhibits the sintering of Ag, but Zn distillates are evolved from Ag-ZnO anodes at cell operating temperatures¹; and, therefore, no long-term benefit would be realized from ZnO.

3. Copper

Copper has been studied as an anode^{1,4,10,11,16} and cathode^{29,30,31,39,46} material in molten carbonate fuel cells; but, in general, very little detail has been published on its performance. In several

experiments Cu powder was mixed with Fe and Ni powders^{1,11} and tested as an anode; for these cells, the cells contained either a mixture of CuO and Cu^{29,30} or Ag, Cu₂O, and ZnO.³¹ Fuel cells operated with CuO-Cu cathodes showed similar performance to that of cells operated with Ag cathodes.^{29,30} Cells having cathodes of CuO mixed with 10 wt % Cu powder and operated at 993 K in a CO₂/air gas mixture could deliver 250 mA/cm² after an endurance run of 27 days. Baker *et al.*⁴⁵ mentioned that Cu is a possible replacement for Ag in the cathode, but only limited developmental work has been reported.⁴⁶

Theoretical calculations⁴⁷ and experimental measurements⁴⁸ have shown that CuO is less soluble than Ag in molten carbonates. In the eutectic Li₂CO₃-Na₂CO₃ melt at 1000 K in a CO₂ gas (1 atm), the solubilities of Ag⁺ and Cu⁺⁺ expressed in mole fraction are 50×10^{-5} and 1×10^{-5} , respectively. In a cell operated at 973 K for 3600 h, Marianowski⁴⁶ found that cathodes of Cu fibers yielded reasonably stable performance (60 mA/cm² at 0.7 V); however, the solubility of Cu in molten carbonates is sufficiently high so that long-term application of Cu cathodes does not appear to be practical⁵⁴. Gorin and Recht⁵⁷ also reported that Cu-CuO cathodes have low lifetimes.

4. Cobalt

Broers^{1,4} and Moss and Gibbens²⁷ considered Co as a potential anode. Broers reported that the activity for CO oxidation decreased in the order Pt>Ni>Co in a molten carbonate fuel cell at 973 K. On the other hand, the measurements of Moss and Gibbens showed that, at 923 and 1023 K, Co was more active than Pt or Ni for CO oxidation. This contradiction in CO oxidation findings is probably due to the differences in the electrode structures and cell designs used by the two groups of investigators; Broers used porous metal powder electrodes and Moss and Gibbens used wire gauze electrodes.

Post-test analysis by Moss and Gibbens²⁷ of their fuel cells showed that the Co wires darkened, increased in diameter, and became brittle. These observations suggest that Co may be subject to corrosive attack by the electrolyte, depending on operating conditions. Moss and Gibbens did not provide any other details with which we can assess the corrosion resistance of Co in molten carbonate fuel cells, but recent studies, discussed later, indicate that Co is a promising anode material.

5. Nickel

Nickel electrodes were probably first tested in molten carbonate fuel cells by Broers.¹ Since then, numerous researchers have tested Ni containing anodes^{2,4,9-11,16,18-23,26-31,33,36-41,43,46,49,51} and cathodes.^{2,19,21,39,50,51} These studies have led to the extensive use of Ni anodes and NiO cathodes in the molten carbonate fuel cell programs funded by DOE and EPRI.

In the reducing environment of a fuel gas in a molten carbonate fuel cell, Ni anodes are thermodynamically stable, except when the polarization exceeds about 200 mV where oxidation to NiO occurs³⁷. Argano *et al.*³⁶ reported that the electrochemical oxidation of Ni to NiO in 80% H₂-20% CO₂ occurs at about 700 mV with respect to a reference electrode fed with a gas mixture of 15% O₂, 30% CO₂, and 55% N₂. In addition to electrochemical oxidation of Ni anodes, carburization of Ni may also be a problem in gases rich in CO³; this problem can be avoided by the addition of sufficient water to the fuel gas.

Nickel cathodes are rapidly oxidized *in situ* to NiO by cathode gases at operating temperature (~ 923 K). According to Gorin and Recht², NiO is completely resistant to corrosion in a molten carbonate fuel cell; however, the longest period of cell operation has been only 14 days. Millet and Buvet³⁴ also reported that NiO is resistant to corrosion in molten carbonates. Nickel oxide is an electronic insulator and, therefore, must be doped with Li ions to produce an electronic conductor which is useful as a cathode. The Li-doped NiO cathode has been obtained by *in situ* reaction of NiO with Li ions and by fabrication of lithiated NiO cathodes prior to assembly in the fuel cell.^{2,34} Austin⁵⁵ described the procedure used by Gorin and Recht to obtain lithiated NiO (1 to 2 mol % Li) cathodes. The presence of stainless steel corrosion products, presumably from current collectors or cell housings, was reported⁵⁶ to destroy the conductivity of the lithiated NiO.

A major problem with Ni anodes is their rapid sintering at operating cell temperatures^{29,35}. A commercially available porous Ni anode (70% porosity) tested in a molten carbonate fuel cell for 625 h at 973 K was found by Broers and Schenke²⁹ to have been reduced in thickness from 1 to 0.6 mm and decreased in geometric surface area by about 30%. Recent developments arising from research on the sintering of Ni anodes indicate that a solution to this problem is available; these findings are discussed later.

6. Noble Metals

Various noble metals such as Au^{21,49}, Pt^{4,16,27,39,50,53}, Pd^{32,39,42,53} and Pd-Ag alloys^{24,26,30} have been used as electrodes in molten carbonate fuel cells. The corrosion resistance of these materials to molten carbonates is considerably greater than that of the other metals (Fe, Co, Ni, Ag, and Cu) considered for use as fuel cell electrodes; however, the cost of the noble metals is prohibitive for electrode application. Data were not found in the literature on the sintering behavior of the above-mentioned noble metals at fuel cell operating temperature (~ 925 K).

7. Alloys Containing Nickel

Stainless steel alloys^{2,9,10,17,20,21,34,50} have been used as electrodes in molten carbonate fuel cells. Gorin and Recht² reported that stainless steel (Type 316) does not show sufficient corrosion resistance for practical application as anodes. Broers^{9,10} operated a molten carbonate fuel cell (at 973 K with an anode consisting of an inconel sieve) that showed a rapid performance decay in 400 h; no reason was given for this decay. Douglas²¹ examined anodes of stainless steel (Type 431) in a fuel cell operated at 873 K with a fuel gas of CO, but insufficient information was presented to assess the corrosion stability of this stainless steel in molten carbonates. Experience with molten carbonate fuel cells by Dezubay²⁰ indicated that anodes of stainless steel have a very limited useful life. These results indicate that stainless steel is probably not a suitable anode material.

Stainless steel has also been used as cathodes^{2,17,20,34,50}. Warren¹⁷ and Dezubay²⁰ reported that stainless steel oxidizes and corrodes in the presence of the oxidant gas in the fuel cell. Furthermore, Warren reported that the electrode was non-conducting after oxidation. On the other hand, Millet and Buvet³⁴ used stainless steel (NS 30) as a cathode for 100 h with no apparent corrosion; and, although initially having a low conductivity,

the electrode became conductive after reaction with lithium ions from Li_2CO_3 . From their fuel cells tests, Gorin and Recht⁷ concluded that cathodes of stainless steel were not suitable due to corrosion in molten carbonates. Except for the observations of Millet and Buvet, it would appear that stainless steel is not suitable as a cathode for extended use in molten carbonate fuel cells.

B. Electrode Structures

The electrodes currently used in the programs on molten carbonate fuel cells funded by DOE and EPRI generally have sintered porous structures of Ni or Ni containing alloy powders. Prior to the DOE and EPRI programs, a wide variety of electrode structures was considered; these structures are summarized in Table 2 along with their reported physical properties.

The electrode structure listed in Table 2 that has been most widely used appears to be the ones formed by sintering of porous metal powders either *in situ*^{1,3,10,17,30} or prior to cell assembly.^{9,10,14,20,21,25,29,30,33,39} Electrode structures sintered *in situ* are formed by applying a thin layer of loose metal powder to the faces of the electrolyte disc at room temperature, and then, at cell operating temperature, the metal particles sinter together. For electrodes sintered prior to fuel cell assembly, the loose metal powder is usually heated in a mold at elevated temperatures (900 to 1200 K) to form a consolidated porous structure. Although the physical descriptions of the sintered electrode structures that have been reported in the literature are rather limited, it appears that the mean pore size is higher and the surface area is lower than those of the porous electrodes currently used in the DOE and EPRI programs.

As noted in Table 2, other electrode structures used in fuel cell tests include wire gauzes, screens, foils, films, and brushes. In general, these electrode structures have surface areas that are probably too low to produce the performance characteristics obtained with the present generation of porous electrodes in molten carbonate fuel cells.

Numerous studies on the oxidation of hydrogen and the reduction of oxygen with solid electrodes in tests of half cells in molten carbonate electrolytes have been reported in the Russian literature. In general, the electrodes reported in these studies are in the form of flat sheets, wires, or rods immersed into a molten carbonate bath. The observations were usually reported with electrodes of Pt⁵⁸⁻⁶², Pd^{59,60,62,63}, Au^{62,63}, and Ag.^{62,63,64} Owing to their prohibitive costs, these materials are not practical for electrodes in commercial molten carbonate fuel cells.

Chudoba and Kubas examined the cathodic reduction of O_2 and CO_2 on electrodes of solid rods of Ag-Al⁶⁵, Ag-Zn⁶⁵, Cu⁶⁶, and Cu-Al⁶⁶ in the molten ternary carbonate eutectic at 850 K. Although the addition of small amounts of Al and Zn improved the performance of Ag and Cu cathodes, these alloys are not considered to be practical for long-term use in molten carbonate fuel cells due to the cost of Ag and the rapid sintering of Cu.

A detailed search of the patent literature on electrodes for application in molten carbonate fuel cells was not conducted for the present survey. Interested readers are directed to Refs. 67-72, which are reviews of the patent literature on electrodes for fuel cells.

Table 2. Characteristics of Electrodes for Molten Carbonate Fuel Cells

Electrode Material	Electrode Structure	Physical Characteristics	Reference
Fe, Co, Ni, Ag Co, Cu, Au	Powder	Layer of powder <0.5-mm thick sintered <i>in situ</i> at cell temperature	1
Ag	Gauze	80 mesh	3, 5
Ni, Fe Inconel	Sintered structure or loose powder	Presintered coherent layers of about 1-mm thickness	9, 10
Ag	Powder	Powder impregnated into Ag screen	9, 10
Ni	Brush	Wire brush of 360 single wires of 0.5-mm diameter and 5-mm length	9, 10
Ni	"Flaked"	<44 μm particles	11
Ag-ZnO	Porous powder	Layer of powder 0.5 mm thick	12, 13
Ag	Sintered powder	Dual porosity electrode prepared by sintering layers of -80 + 100 mesh and -20 + 40 Ag powders at 1123 - 1193 K for 1 h in N_2	14
Ni-Cr	Porous layer	Flame-sprayed layer (0.5-mm thick)	17
Ag	Porous layer	Flame-sprayed	17
Ag	Film	Painted with Ag_2O and reduced to Ag <i>in situ</i>	17
Ni, Ag	Sintered powder	1.5-mm thick and 10 μm pore size, or dual layer having 5 μm and 15 μm pore sizes	20

(Cont'd)

Table 2. (Cont'd)

Electrode Material	Electrode Structure	Physical Characteristics	Reference
Ni	Powders sintered at 973 K	34% porosity, 10-50 μm pore size, 190 cm^2/g	21
Ni	Powders sintered at 973 K	40% porosity, 10-30 μm pore size, 950 cm^2/g	21
Ag	Powders sintered at 973 K	42% porosity, 1-50 μm pore size, 75 cm^2/g	21
Ag	Powders sintered at 973 K	50% porosity, 1-20 μm pore size, 500 cm^2/g	21
Au	Powders sintered at 973 K	62% porosity, 1-10 μm pore size, 340 cm^2/g	21
431 SS	Powders sintered at 973 K	18% porosity, 10-50 μm pore size	21
Pd-Ag	Foil	75 μm thickness	24
Ag	Film	Ag painted onto electrolyte disc	24
Ag	Sintered powder	Electrodes made from sintered powders (3 to 20 mesh or -325 mesh)	25
Ag	Gauze	60 mesh	27
Co, Ni, Pt	Wire screen	37 s.w.g. wires	27
Ni	Wire screen	120 mesh	28
Ag-plated SS	Wire screen	120 mesh	28
Cu-CuO	Sintered at 1073 K	1 mm thickness	29, 30
Ag	Wire screens and/or thin layer of powder	≤ 0.1 mm thickness	29, 30

(Cont'd)

Table 2. (Cont'd)

Electrode Material	Electrode Structure	Physical Characteristics	Reference
Ni	Sintered powder	-100 + 200 mesh powder sintered <i>in situ</i> to structure 50% porosity and 1 mm thickness	31
Ag-Cu ₂ O-ZnO	Sintered powder	-100 + 200 mesh powder sintered <i>in situ</i> structure 50% porosity and 1 mm thickness	31
Ag	Porous layer	Flame-sprayed layer 0.1 mm thickness	32
Ni	Sintered powder	Ni particles sintered on 120 mesh Ni screen	33
Ag	Sintered powder	Ag particles sintered on 120 mesh Ag-plated SS	33
NS 30 SS	Sintered powder	10 μ m average pore size	34
Li ₂ O-doped NiO	Sintered powder	Heat powder to >1473 K	34
Pd or Pd-Ag	Foil	30 to 50 μ m thickness	34
Ag	Film	Painted on electrolyte disc	36, 37
Ni	Fiber felt	80% porosity, 30-100 μ m pore size, 760 μ m thickness	36, 37
Ni	Sintered powder	3 to 70 μ m particles of Ni sintered on Ni screen	39
Cu	Sintered powder	30 to 40 μ m particles of Cu sintered on SS screen	39
Ag	Film	10 μ m thickness	45
Ni	Fibers	38 to 85% porosity	45
Ni	Fibers	80% porosity, 0.75-mm thickness	46
Cu	Fibers	80% porosity	46

III. AGING AND DEGRADATION OF MOLTEN CARBONATE FUEL CELL ELECTRODES

The results of the survey on the aging and degradation of electrodes due to corrosion, sintering, and contamination are discussed below.

A. Corrosion of Electrode Materials

Because of the corrosive nature of molten carbonate electrolytes, considerable effort has been directed towards examining the corrosion behavior of metals and alloys that are used as electrodes in molten carbonate fuel cells. The desired operating life for a commercial molten carbonate fuel cell is 40,000 h, which requires that electrode materials possess extremely high electrochemical/chemical stability to the molten salt and the gas-phase environment. In many instances, fuel-cell tests reported in the literature were terminated due to corrosion of the electrode. The corrosion stability of electrode materials used in molten carbonate fuel cells has been examined theoretically, by a thermodynamic treatment, and experimentally.

1. Thermodynamic Considerations

A simplified potential scale, E° , was calculated by ICT⁸ from the equation $\Delta G^\circ = -nFE^\circ$ (ΔG° is the Gibbs free energy, n is the number of electrons, and F is the Faraday constant), which gives a qualitative indication of the stability of a metal in the reduced or oxidized state. These results are given in Table 3 for the electrode materials discussed in Section II. The standard electrode potentials were calculated from free energies determined by linear extrapolation of standard free energies to the approximate fuel cell operating temperature of 925 K. If a value of zero volt is arbitrarily assigned to the O_2/O^{2-} redox couple in each of the reactions, the potential of the hydrogen reaction is -1.019 V. Any anode metal with a potential less negative than -1.019 V will tend to be in the reduced metallic form, while metals with potentials more negative will be in the oxidized form. Thus, metals such as Co, Ni, Cu, Ag, and the noble metals will tend to be in the reduced, metallic state as anodes in molten carbonate fuel cells. However, high anode polarization may lead to oxidation of the metal; this has been observed experimentally³⁷ with Ni, for example.

A thermodynamic approach to the analysis of stability and corrosion behavior of metals in molten carbonates has been presented by Ingram and Janz,⁷³ who adopted the thermodynamic concepts developed by Pourbaix⁷⁴ to analyze the corrosion of metals in aqueous solutions. Pourbaix used thermodynamic data to construct diagrams in which the redox potential (E) of a metal is plotted versus the pH of the aqueous solution. Similar-type of diagrams were constructed by Ingram and Janz for molten carbonate electrolytes by use of a function, analogous to pH, which expressed the acidity of the molten salt system. Since the dissociation of the carbonate anion gives rise to well-defined acid/base behavior,

the acidity of the melt was expressed as pO^{2-} ($= -\log_{10} [O^{2-}]$) or as pCO_2 ($= -\log_{10} [CO_2]$). According to the authors, the latter function seems to have the greater practical usefulness because the presence of CO_2 is usually fixed by the experimental conditions.

The construction of a potential vs $p\text{CO}_2$ diagram can be described best by way of an example. Ingram and Janz⁷³ plotted the dependence of E_{redox} on $p\text{CO}_2$ for Ni in a ternary eutectic of the alkali carbonates (Li:Na:K = 43.5:31.5:25 mol %) at 873 K (see Fig. 1). The diagram is divided into three regions in which only one nickel phase may be present at unit activity: Ni metal, Ni^{2+} , or solid NiO. The boundaries between the three phases were calculated from thermodynamic data.

In Fig. 1, the boundary between Ni^{2+} and Ni metal depends on the redox potential and the standard potential of Ni (potential of $\text{CO}_2:\text{O}_2 = 2:1$ mixture set equal to zero). For the cell reaction,

Hence,

$$E^\circ_{\text{Ni}/\text{Ni}^{2+}} = -0.34 \text{ V}$$

and

$$E_{\text{redox}} = -0.34 + 2.3 \frac{RT}{2F} \log [\text{Ni}^{2+}]$$

The boundary separating the domains of Ni^{2+} and Ni metal in Fig. 1 represents E_{redox} at a Ni^{2+} activity equal to one. The boundary between the domains for Ni^{2+} and NiO is the value of $p\text{CO}_2$ when NiO precipitates from a pure NiCO_3 melt. For the reaction,

Hence,

$$K_d = \frac{[\text{NiO}] [\text{CO}_2]}{[\text{NiCO}_3]} = 10^{5.24}$$

and

$$\begin{aligned} \log [\text{Ni}^{2+}] &= -\log K_d - p\text{CO}_2 \\ &= -5.24 - p\text{CO}_2 \end{aligned}$$

At the boundary separating the domains for Ni^{2+} and NiO, $\log [\text{Ni}^{2+}] = 0$.

When the oxygen pressure is reduced to below the dissociation pressure of NiO ($10^{-19.2}$ atm), the analysis indicates that Ni metal may appear. In Fig. 1, the value of the dissociation pressure, $\log P_{\text{O}_2} = -19.2$, sets the boundary between the NiO and Ni phases and is plotted on the outer frame of the diagram.

Fig. 1. Potential vs $p\text{CO}_2$ for the System Nickel-Ternary Carbonate Eutectic at 873 K⁷³

For aqueous systems, Pourbaix⁷⁴ made the arbitrary assumption that a metal would corrode if the equilibrium concentration of its ions in solution was greater than 10^{-6}M ; if less, the metal was said to be immune. This assumption was also applied by Ingram and Janz⁷³ to determine the corrosion boundary of metals in molten carbonates, which is represented by the dashed lines in Fig. 1. On the diagram in Fig. 1 Ni metal immersed in a carbonate melt under 1 atm total pressure of CO_2 (2/3 atm) and O_2 (1/3 atm) would be at a potential close to zero and a nickel ion concentration close to 10^{-5}M . According to Ingram and Janz,⁷³ the thermodynamic treatment for this situation indicates that either the metal will corrode completely to oxide, or the NiO will form a coherent film on the metal surface and lead to passivation; experimental data are required to determine which of these two possibilities occur.

Thermodynamic data for Fe, Ag, Au, and Pt were used by Ingram and Janz⁷³ to calculate potential vs $p\text{CO}_2$ diagrams for these metals in molten carbonates at 873 K; the diagrams are presented in Figs. 2, 3, 4, and 5, respectively. Ingram and Janz considered the case where the metal is immersed in molten carbonate under 1 atm total pressure of CO_2 (2/3 atm) and O_2 (1/3 atm) and concluded from the diagrams presented in Figs. 2 through 5 that Pt and Au should be immune from corrosion, Ag should corrode, and Fe may exhibit passivation if the oxide forms a coherent film.

Fig. 2. Potential *vs* $p\text{CO}_2$ for the System Iron-Ternary Carbonate Eutectic at 873 K⁷³

Fig. 3. Potential *vs* $p\text{CO}_2$ for the System Silver-Ternary Carbonate Eutectic at 873 K⁷³

Fig. 4. Potential vs $p\text{CO}_2$ for the System Gold-Ternary Carbonate Eutectic at 873 K⁷³

Fig. 5. Potential vs $p\text{CO}_2$ for the System Platinum-Ternary Carbonate Eutectic at 873 K⁷³

2. Experimental Studies

Many investigators have studied the corrosion behavior of a variety of metals and alloys considered for use as fuel cell electrodes and cell components; some of these studies were discussed in a comprehensive review by Klein.⁷⁵ Results from fuel cell tests and from simulated cell tests in the laboratory, which were reviewed by Klein, have shown that only a very limited number of metals and alloys exhibit sufficient corrosion resistance in molten carbonate to be suitable as fuel cell electrodes. Experimental data from these studies are discussed below. The corrosion behavior of the noble metals is not discussed because they are too expensive for electrodes in molten carbonate fuel cells.

a. Iron

Of the metals discussed, Fe appears to be the most susceptible to corrosive attack by molten carbonate. Degobert and Bloch⁷⁶ reported the following order of decreasing nobility of metals at 873 K in ternary eutectic carbonate in CO₂:

10% Ir-Pt alloy > 10% Rh-Pt alloy > Pt > Pd > Au > Ag > Cu > C > Co > Ni
 > stainless steel (18% Cr-8% Ni) > Fe

This order of corrosion stability was determined from current vs voltage curves obtained by a potentiostatic technique. Davis and Kinniburgh⁷⁷ estimated the corrosion rate, by a potentiostatic technique, of an iron wire in a Li₂CO₃-Na₂CO₃ eutectic at 953 K. They found that the corrosion rate was high--105 mm/yr at -850 mV and 525 mm/yr at -100 mV with respect to a O₂:CO₂ = 1:2 reference electrode. This result indicates that iron is unsuitable as an electrode material in a molten carbonate fuel cell. In comparison, the estimated corrosion rates for Ni at -850 and -100 mV were reported to be 0 and 29.4 mm/yr, respectively.

b. Silver

Janz and co-workers⁷⁸⁻⁸⁰ have also examined the corrosion stability in molten carbonate of many of the metals listed above. They determined the following decreasing order of nobility in the ternary eutectic carbonate 873 K in CO₂:

20% Pd-Au alloy > Au > Pt > Ag > Ni

The steady-state or corrosion potential with respect to a Ag/Ag⁺ reference half-cell electrode for this series of metals at 873 K are as follows: -430 mV for 20% Pd-Au alloy, -470 mV for Au, -475 mV for Pt, -680 mV for Ag, and -1166 mV for Ni.

Although Ag appears to be more noble than Ni in molten carbonate, experimental evidence in fuel cell tests^{21,32-34} and in laboratory pot tests^{34,48,77,81-83} showed that Ag has an appreciable solubility in molten carbonates. Douglas²¹ observed that, within 100 h, a fuel cell containing a Ag cathode had about one gram of Ag deposited on the anode in the form of small crystals. If growth of Ag on the anode were to continue, an electronic

short circuit between the electrodes is conceivable. Salvadori³² reported that some progress was made to reduce the corrosion of Ag by adding refractory oxides to the electrolyte or to the cathode itself, but these cathodes were only operated for a few hundred hours. With the use of a so called "paste electrolyte". Schenke and Broers²⁹ concluded that the corrosion rate of Ag cathodes is small, and significant Ag deposition on the anode is prevented. Their experience has shown that the overall corrosion rate of practical cathodes in paste electrolyte cells operating at 993 K and 100 mA/cm² is probably less than 20 mg/cm² per year. However, because appreciable Ag corrosion is unavoidable in molten carbonate, the Ag cathode is precluded for long-term operation. The cost of Ag is also prohibitive for commercial fuel cell application.

Measurements have been made on the solubility of Ag in molten carbonates. Janz *et al.*⁷⁸ reported a value on the order of 1-2 mg of Ag in 60 g molten carbonate (ternary eutectic) at 900 to 1200 K. In equimolar Li₂CO₃-Na₂CO₃, the saturation concentration of Ag⁺ at 823 K was reported by Bartlett and Johnson to be 0.13 M in a CO₂ + O₂ environment.³¹ Finally, experimental weight-loss measurements made by Trachtenberg and Cole⁸³ showed that corrosion of Ag is increased by raising the O₂ partial pressure in the cathode gas supply; Ag was not corroded with CO₂ alone.⁸¹

c. Copper

Experimental data available in the literature⁴⁸ indicate that CuO dissolves in molten carbonates, but the solubility is lower than that of Ag. Copper is considerably less costly than Ag and would, therefore, be an attractive material for the cathode in a molten carbonate fuel cell; however, the solubility of CuO in the electrolyte limits its use.⁵⁴ On the other hand, Cu would be in the reduced metallic state (see Table 3) in the fuel gas environment and might be suitable as an anode if sintering can be avoided.

d. Cobalt

Only limited data were found in the literature on the corrosion of Co in molten carbonates. According to Bartlett and Johnson,^{81,84} Co is not corroded by pure, dry carbonate melts at 827 K. The results reported by Drossbach and Sauermann⁸⁵ indicate that the decreasing order of nobility of metals in the ternary carbonate melt under CO₂ at 873 K is

The data obtained by Degobert and Bloch⁷⁶ showed that Co was more noble than Ni in the ternary eutectic at 873 K; and the recent cell tests with Co anodes at IGT⁸⁶ indicated that no apparent corrosion was present, but that sintering occurred.

e. Stainless Steel

Various types of stainless steels have been considered as materials for electrodes and other cell components such as a current collector or cell housing. Corrosion studies by Janz *et al.*^{79,87} on type 347 (niobium-stabilized) and type 304 stainless steels in the ternary carbonate

Table 3. Standard Electrode Potentials at 925 K⁸

Material	Reaction ^a	Electrode Potential, V
Au	$2\text{Au (c)} + 3/2 \text{O}_2 \text{ (g)} = \text{Au}_2\text{O}_3 \text{ (c)}$	0.422
Ag	$2\text{Ag (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{Ag}_2\text{O (c)}$	0.144
Pt	$\text{Pt (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{PtO (c)}$	0.043
Pd	$\text{Pd (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{PdO (c)}$	0.011
Cu	$\text{Cu (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{CuO (c)}$	-0.389
Ni	$\text{Ni (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{NiO (c)}$	-0.802
Co	$\text{Co (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{CoO (c)}$	-0.871
H	$\text{H (g)} + 1/2 \text{O}_2 \text{ (g)} = \text{H}_2\text{O (g)}$	-1.019
C	$\text{CO (g)} + 1/2 \text{O}_2 \text{ (g)} = \text{CO}_2 \text{ (g)}$	-1.05
Fe	$\text{Fe (c)} + 1/2 \text{O}_2 \text{ (g)} = \text{FeO (c)}$	-1.06
Cr	$\text{Cr (c)} + \text{O}_2 \text{ (g)} = \text{CrO}_2 \text{ (c)}$	-1.13
Zn	$\text{Zn (l)} + 1/2 \text{O}_2 \text{ (g)} = \text{ZnO (c)}$	-1.32
Ti	$\text{Ti (}\alpha\text{)} + \text{O}_2 \text{ (g)} = \text{TiO}_2 \text{ (c)}$	-2.01
Zr	$\text{Zr (}\alpha\text{)} + \text{O}_2 \text{ (g)} = \text{ZrO}_2 \text{ (c)}$	-2.38
Al	$2\text{Al (c)} + 3/2 \text{O}_2 \text{ (g)} = \text{Al}_2\text{O}_3 \text{ (cor)}$	-2.39
Li	$2\text{Li (l)} + 1/2 \text{O}_2 \text{ (g)} = \text{Li}_2\text{O (c)}$	-2.44

^aSymbols: c is crystalline, α is α phase, and cor is corundum.

eutectic at 873 to 973 K in dry CO₂ showed that these steels passivated in the molten salt. The corrosion potential for both steels at 873 K, referred to a Ag/Ag⁺ reference half-cell, is -525 ± 30 mV. The corrosion potential of Ag and Ni are -680 and -1166 mV, respectively, on the same scale. Thus, the decreasing order of nobility at 873 K is

stainless steel > Ag > Ni

Janz and Conte⁷⁹ reported the presence of a LiFeO₂ film, detected by X-ray diffraction analysis, to be responsible for the corrosion resistance of these stainless steels in molten carbonate. However, experiments by Grantham and Ferry⁸⁸ on the corrosion of type 347 stainless steel in the ternary carbonate eutectic suggested that a dense, protective film of LiCrO₂ was formed which is protective up to 973 K. The similarity of the X-ray diffraction patterns of LiFeO₂ and LiCrO₂ may possibly explain the discrepancy in the identity of the passive film by the above two groups of investigators. Millet and Buvet³⁴ have also reported that stainless steel (type NS30) is protected from corrosion in molten carbonate (ternary eutectic at 873 K) by a protective layer, but this layer was not identified in their publication.

Despite the above reports that stainless steels are protected from corrosion by a passive oxide film, results from fuel cell tests^{2,9,10,17,20,56} with stainless steel electrodes have not been encouraging; poor performance and corrosion have been reported with fuel cells containing stainless steel anodes or cathodes. Recently, the General Electric Company (GE)⁸⁹ has re-examined the use of stainless steel as an anode in a molten carbonate fuel cell; the stainless steel was oxidized in the fuel gas environment (24% CO₂-34% H₂-42% N₂). Cell (CRD-017) performance was found to deteriorate rapidly with time, the output current at a constant cell voltage of 0.7 V being decreased from 1.02 to 0.30 A in 15 h. No explanation was given for the rapid decrease in cell performance with time. After termination of the cell test in 48 h, the stainless steel showed signs of only slight corrosion, indicated by a darkened surface.

f. Nickel

Since about 1970, Ni has been the primary metal used in anodes and cathodes of molten carbonate fuel cells. Thermodynamic calculations (see Table 3 and Fig. 1) show that Ni in the fuel gas environment is present as the reduced metal; this result has been verified in molten carbonate fuel cells operating at low anode polarizations (<200 mV). Johnson⁸⁴ reported that Ni was not corroded by pure, dry carbonate melt (Li₂CO₃-Na₂CO₃ eutectic) at 827 K. Davis and Kinniburgh⁷⁷ estimated that the corrosion rate of Ni in the binary Li₂CO₃-Na₂CO₃ eutectic at 953 K is 0 and 29.4 mm/yr at -850 mV and -100 mV, respectively, referred to a half-cell reference electrode (O₂:CO₂ = 1:2). These data were estimated from transient measurements of potentiostatic polarization curves of Ni immersed in the carbonate melt and, therefore, are not necessarily representative of the long-term corrosion rate of Ni in a molten carbonate fuel cell.

Since Ni is oxidized to NiO at the cathode, long-term stable operation of molten carbonate fuel cells (containing cathodes of Ni) depends, to some extent, on the chemical stability of NiO. Gorin and Recht² reported that NiO was completely corrosion resistant in molten carbonate fuel cells, but their observation was based on tests that lasted only 14 days. Bacon⁹⁰ found that the corrosion resistance of dual porosity Ni electrodes in alkaline fuel cells could be significantly improved by soaking these electrodes in LiOH solution followed by heating in air to 973 K. This treatment produced a thin surface layer of lithiated-NiO which had a very low concentration of cation vacancies compared to pure NiO; and, therefore, the NiO was thought to be more corrosion resistant. Conceivably, the corrosion resistance of NiO cathodes in molten carbonate fuel cells could also be improved by doping with Li cations, but no data are available to verify this hypothesis.

Cell-endurance tests of up to 7000 h did not appear to be limited by problems with a NiO cathode.⁵¹ Post-test analysis of cells operated for ~700 h with NiO cathodes showed evidence of a NiO diffusion layer in the electrolyte structure on the cathode side.⁹¹ Although the mechanism by which NiO was transported into the electrolyte structure is not clearly understood, it is conceivable that mechanical compression of the cell components forced the NiO to embed into the electrolyte structure. Since the thickness of the diffusion layer of NiO did not appear to show any relationship to the number of hours of cell operation, the dissolution of NiO in the molten carbonate and subsequent deposition in the electrolyte

structure is apparently not important in these experiments. However, the solubility of NiO in the electrolyte could conceivably affect the long-term stability (up to 40,000 h) of the NiO cathode and ultimately cell performance. A systematic study of the solubility of NiO in molten carbonates would be helpful to assess this effect on long-term cathode performance.

Other technical problems with NiO cathodes in molten carbonate fuel cells have been discovered. In general, the NiO cathode is formed by the *in situ* oxidation of porous Ni electrodes. This procedure results in poor control of the physical properties (such as porosity, pore size distribution, and mean pore size) of the oxidized Ni structure; consequently, matching of the electrode pore structure to the pore distribution in the electrolyte matrix, which is necessary to achieve good cell performance,⁹² is difficult. Furthermore, the structure of the NiO formed *in situ* possesses poor mechanical integrity and, therefore, is susceptible to further degradation in a cell. To improve the mechanical strength of the cathode, Energy Research Corporation (ERC) has examined the use of a stainless steel screen as reinforcement. A cell (S7-3) with a reinforced cathode⁹⁴ showed stable performance for about 1400 h at 923 K. After 1900 h the cell was disassembled; no analysis of the cathode structure was reported at that time.

A practical problem is encountered with *in situ* oxidation of Ni to NiO to form the cathode because the volume increases (~30%) upon oxidation; therefore, space must be reserved in the cell to accommodate this expansion. Although this expansion may not be a severe problem in laboratory scale cells, stack design will probably require that the NiO cathode be formed prior to assembly into the cell. Examination of procedures to manufacture sintered NiO electrodes merit consideration.

Nickel oxide is a p-type semi-conductor which must be made conducting in order to serve as an useful cathode. In the fuel cell, the conductivity of NiO is enhanced by doping with Li from Li₂CO₃ in the molten carbonate electrolyte. The incorporation of Li₂O into NiO involves oxidation of Ni²⁺ to Ni³⁺ by a reaction such as

By doping a pellet of NiO at 973 K with 3.4 at. % Li, More and White^{95,96} increased the conductivity from 0.034 ohm⁻¹ cm⁻¹ to 47 ohm⁻¹ cm⁻¹. A detailed discussion on the electron conduction mechanism of NiO and Li-doped NiO is outside the scope of the present review, but has been considered in other publications.⁹⁷⁻¹⁰⁴ The conductivity of NiO increases with an increase in the concentration of Li^{96,100-102} and the oxygen pressure;^{98,103,104} however, impurity ions^{99,105} such as Fe³⁺ and Cr³⁺ cause a decrease. The introduction of Fe³⁺ in Li₂Ni_{1-x}O has a poisoning effect which decreases the electrical conductivity since fewer Ni³⁺ ions are formed due to the formation of Li⁺-Fe³⁺ pairs;⁹⁹ a similar effect would be expected with the presence of Cr³⁺. Since stainless steel is commonly used in cell components, any corrosion products containing Fe³⁺ and Cr³⁺ would have an adverse effect on the conductivity of the cathode, if these ions were introduced into the NiO structure. Apparently, the decrease in conductivity of Li₂O-doped NiO by a stainless steel corrosion product

was noted by Austin,⁵⁶ but no further details were given. Further studies are warranted to determine the effect of impurities on the conductivity of Li-doped NiO cathodes and to develop methods to improve the conductivity of NiO in molten carbonate fuel cells.

3. Effect of Electrolyte Composition

The above discussion reported on the corrosion of metals in "acid" molten carbonates. The term "acid" is used to denote a carbonate melt under a relatively high CO₂ pressure. On the other hand, a "basic" molten carbonate is one where relatively large quantities of oxide (hydroxides) are present in the melt; this is the case in gas environments containing H₂O or without CO₂. In a fuel cell operating at high oxidant or fuel utilization (~80%, for example), the formation of "basic" molten carbonates is likely. Thus, the investigation of the corrosion behavior of electrode materials in "basic" molten carbonates is desirable to simulate realistic conditions for corrosion in operating fuel cells; but, unfortunately, experimental studies under these conditions are scarce.

Anderson¹⁰⁶ has reviewed the literature on the corrosion of metals in "acid" and "basic" molten carbonates, and also investigated the corrosion of Ag, Au, Pd-80% Au alloy, Pt, and refractory oxides in "basic" molten carbonates and sodium oxide. His studies showed that the corrosion rate of Au in molten Na₂O is a factor of 10 or more larger than that found in a Na₂CO₃-K₂CO₃ melt with 5 mol % Na₂O, and it is 10⁴ larger than that in a Li₂CO₃-Na₂CO₃-K₂CO₃ melt with 1 mol % Na₂O. The corrosion rate of Ag in "basic" molten carbonates is about one-fourth that of Au at the same conditions.

Experiments by Cohen-Adad *et al.*¹⁰⁷ with Ni and Pt in M₂CO₃-MOH (where M = Li, Na, K and Rb) showed that these metals are corroded in "basic" molten carbonates. Bunzel and Kohlmeyer¹⁰⁸ conducted corrosion studies in molten Na₂O, and found that metal oxides (BeO, ZrO₂, ThO₂, MgO, Al₂O₃, and NiO) and metals alone (Fe, Co, Ni, Cu, W, Mo, and Al) were severely corroded by Na₂O.

A better understanding of the corrosion rate (and solubility) of NiO, which is presently the leading candidate as the cathode in "basic" molten carbonates, is desirable to predict the long-term stability of NiO in operating fuel cells. In addition, the effect of impurities (such as halogen- and sulfur-containing compounds) on the corrosion of NiO in molten carbonates should be determined. Observations by Grantham and Ferry¹⁰⁹ indicate that sulfur compounds in the carbonate melt enhance corrosion of metals, but that chloride compounds do not alter the corrosion rate markedly. Further studies are necessary to verify these findings under fuel cell conditions.

B. Sintering of Porous Electrodes

In the mid 1960's, Broers^{29,30} observed that fine porous metals sinter together at elevated temperatures common to molten carbonate fuel cells (873-973 K). Thus, he stated that any preselection of anode structure, pore size dimension, and distribution was useless at temperatures of about 973 K. Since the early work of Broers, considerable progress has been made

in the inhibition of the sintering in anode structures. In 1975, King⁵¹ reported that fuel cells operated with proprietary anode structures were stable for at least 7000 h. The improvement in the lifetime characteristics of fuel cells with stabilized anodes over that of cells with conventional Ni anodes is graphically displayed in Fig. 6. In more recent studies sponsored by DOE and EPRI additives to inhibit the sintering of Ni have been identified, and the mechanism by which these additives inhibit the sintering of metals has been studied.

Fig. 6. Improvements in Endurance of Molten Carbonate Cells with Stabilized Anode Structures Reported in 1975 by King. (Used with permission of the Society of Automotive Engineers, Inc. 1975, © SAE.)⁵¹

1. Sintering Mechanisms

The driving force for sintering of a single phase powder is the reduction of the free energy of the system due to a reduction in the solid/vapor (or solid/liquid) surface area, and thus the total surface free energy. A detailed discussion of the various mechanisms that have been proposed to describe the kinetics of powder sintering is outside the scope of the present report since comprehensive reviews on this subject are available elsewhere,¹¹⁰⁻¹¹² but a brief overview seems appropriate.

Three stages have been distinguished in the course of sintering a powder agglomerate to the dense material.^{111,112} These merge continuously into one another, but three distinct features can be readily identified with each stage.

- (a) Neck Growth. During the first stage in the sintering of loose powder masses, the particles, to a large extent, preserve their original shape, but necks form between contacting particles and any voids that are produced are interconnected.
- (b) Densification and Grain Growth. When the ratio of the neck radius to the particle radius exceeds a certain value, the separate particles begin to lose their identity. Most of the shrinkage takes place at this stage, and a coherent network of pores is formed and grain growth continues. When ~90% of theoretical density is exceeded, the relative proportion of closed pore spaces increases rapidly.
- (c) Pore Closure. The isolated pores become increasingly spheroidized. Further densification still proceeds slowly and it is often impossible to decide whether this densification has ended.

The first stage of sintering can be brought about by one or more of the following processes: viscous or plastic flow, evaporation and condensation, and volume diffusion or surface diffusion of atoms. Theoretical investigations by Kuczynski¹¹⁰ led to well known relationships to describe the kinetics of the first stage of sintering:

$$x^n/a^m = F(T)t$$

where x and a are the radii of the neck and sphere, respectively, t is time, and $F(T)$ is a function of temperature. In the above equation, $n = 2$, $m = 1$ for viscous or plastic flow; $n = 3$, $m = 1$ for evaporation and condensation; $n = 5$, $m = 2$ for volume diffusion; and $n = 7$, $m = 3$ for surface diffusion. Sintering experiments with samples of controlled geometry (generally spheres or wires) can be used to determine the values of m and n , thereby permitting one to distinguish between these sintering mechanisms. However, these studies do not always result in an unambiguous definition of the sintering mechanism.

In addition to densification, there are at least three kinds of geometric changes which occur in the course of sintering, and result in a progressive decrease in surface area.¹¹³ These are (1) a change in the surface contour of particles; (2) the conversion of channels to isolated porosity without a change in volume; and (3) a decrease in the number of pores or channels without a change in volume. DeHoff *et al.*¹¹³⁻¹¹⁵ conducted an analysis of the relationship between the decrease in surface area with increase in the densification of metal compacts. DeHoff *et al.*¹¹³ started with the assumption that each gram of material transported to increase the density of the powder requires the expenditure of a fixed amount of energy, independent of the stage to which densification has progressed; and then developed a theoretical expression for the relationship between S_v (surface area per unit volume) and ρ (weight of powder/total volume). The amount of material transported per gram of powder, Δm , is proportional to the total energy expended during that time:

$$\Delta m = k_1 \Delta F \quad (1)$$

where ΔF is the Gibbs free energy due to a decrease in the surface area. In addition,

$$\Delta m = \rho_o (V_o^0 - V^0) \quad (2)$$

where ρ_o is the initial density of the powder, V_o^0 is the initial specific volume, and V^0 is the specific volume at time t . The change in Gibbs free energy per gram of powder is

$$\Delta F = \gamma \Delta A = \gamma (S_{v_o} V_o^0 - S_v V^0) \quad (3)$$

where A is the surface area per gram of powder, γ is the surface free energy, and S_v is the surface area per unit volume. Substituting Eqs. (2) and (3) into (1) gives

$$\rho_o (V_o^0 - V^0) = k_1 \gamma (S_{v_o} V_o^0 - S_v V^0) \quad (4)$$

Since

$$\frac{V_o^0}{V^0} = \frac{\rho}{\rho_o} \quad (5)$$

substituting this relationship into Eq. (4) we arrive at

$$\frac{\rho}{\rho_o} = [S_v - (\rho_o/k_1 \gamma)] / [S_{v_o} - (\rho_o/k_1 \gamma)] \quad (6)$$

where ρ is the density of the sintered powder at time t . Thus, Eq. (1) leads to a proportionality between the density and surface area per unit volume. Experimentally, DeHoff *et al.*^{113,114} observed a linear relationship between the density and the surface area per unit volume, which was expressed as

$$\rho = m S_v + \rho_t \quad (7)$$

where ρ_t is the bulk density of the solid, and m is a system constant.

An equation describing the kinetics of densification was also derived by DeHoff *et al.*¹¹³ As a first approximation, it was assumed that the rate of consumption of energy during sintering is proportional to the surface energy remaining, that is

$$\frac{dF}{dt} = -k_2 F \quad (8)$$

Separating the variables and integrating from zero time gives

$$F = F_o e^{-k_2 t} \quad (9)$$

Substituting Eq. (9) and (2) into Eq. (1) gives

$$\rho_o (V_o^o - V^o) = k_1 (F_o - F_o e^{-k_2 t}) \quad (10)$$

where k_1 is a proportionality constant. For the boundary condition $t = \infty$, $V^o = V_t^o = 1/\rho_t$,

$$k_1 = \rho_o (V_o^o - V_t^o) / F_o \quad (11)$$

Thus, Eq. (10) may be rewritten as

$$\rho_o (V_o^o - V^o) = \rho_o [(V_o^o - V_t^o) / F_o] F_o (1 - e^{-k_2 t}) \quad (12)$$

Upon rearranging Eq. (12), we get

$$(V^o - V_t^o) / (V_o^o - V_t^o) = e^{-k_2 t} \quad (13)$$

Expressing the specific volume in terms of density, we get

$$\left(\frac{1}{\rho} - \frac{1}{\rho_t} \right) / \left(\frac{1}{\rho_o} - \frac{1}{\rho_t} \right) = e^{-k_2 t} \quad (14)$$

which upon rearrangement gives

$$\left(\frac{\rho_t}{\rho} - 1 \right) / \left(\frac{\rho_t}{\rho_o} - 1 \right) = e^{-k_2 t} \quad (15)$$

After substituting the porosity, P , we arrive at

$$(P/1 - P) / (P_o/1 - P_o) = e^{-k_2 t} \quad (16)$$

Experimental data obtained for the sintering of Cu and Ni by DeHoff *et al.*,^{113 114} agree with these theoretical relationships. A review of experimental data on the densification of metal powders during sintering was completed by Thummler and Thomma.¹¹¹

The reduction in surface area with time during isothermal sintering has been examined by German and Munir. A kinetic model was considered which analyzed the time dependence of surface-area reduction during neck growth between two contacting spherical particles. The basic equation developed by Kuczynski,¹¹⁰

$$(x/a)^\alpha = F(T)t \quad (17)$$

was reconstructed to give surface-area reduction for the case of a small neck. For this reconstruction, the surface-area loss with neck growth was approximated as

$$\Delta S = S_o - S \approx \pi x^2 \quad (18)$$

where S is surface area at a neck size of x , and S_0 is the initial surface area. For a compact of spherical particles, the initial surface area per interparticle contact is given by

$$S_0 = 4\pi a^2/N_c \quad (19)$$

where N_c is the particle packing coordination which is related to the green density. Combining Eqs. 17 and 18 and normalizing with respect to S_0 leads to the kinetic equation for surface area reduction:

$$(\Delta S/S_0)^{\alpha/2} = Ct \quad (20)$$

where

$$C = F(T) (N_c/4)^{\alpha/2} \quad (21)$$

By an alternative analysis, German and Munir¹¹⁷ derived an equation similar to Eq. (20)

$$(\Delta S/S_0)^\beta = Kt \quad (22)$$

where K is a constant which is dependent on the sintering mechanism and packing coordination, and the exponent β is related to the sintering mechanism. German and Munir^{116,118} reviewed the sintering data in the literature to verify the kinetic model described by Eq. (22) and also to identify the sintering mechanism.

Equation (22) is applicable to the initial stage of sintering of powder compacts (generally valid up to $\Delta S/S_0 \approx 50\%$). More recently, German¹¹⁹ developed an equation to describe the kinetics of surface-area reduction for the intermediate stage of sintering (during this stage of the sintering cycle, a powder compact approaches the density of the bulk metal); this equation can be expressed as

$$\frac{dS}{dt} = -(B/\delta S_1^\delta) S^{\delta+1} \quad (23)$$

where S is the surface area (volumetric), S_1 is the surface area at the beginning of the intermediate stage, δ is 1.6 to 2.3 depending upon the material, and B is a constant determined by the microstructure. Equation (23) represents the sintering stage where the coalescence and elimination of pores are coupled to grain-growth kinetics.

2. Experimental Studies on Electrode Sintering

a. Nickel

The sintering of porous Ni anodes has been investigated in controlled laboratory tests and in molten carbonate fuel cells. The purpose of these tests was to obtain experimental data to serve as a "benchmark" for comparison with the sintering behavior of stabilized Ni structures and alternative metal electrodes.

The performance of two molten carbonate fuel cells having Ni anodes is illustrated in Figs. 7 and 8, which were obtained from data reported by IGT¹²⁰ and ERC,¹²¹ respectively. In both cell tests, the operating temperature was 923 K. The cell performance in Fig. 7 (Cell DOE-2) shows a marked decrease with time (~ 600 h), while in Fig. 8 (Cell 7-17) the decrease in cell performance with operating time is less, even though the test lasted for 2000 h. With the use of reference electrodes in their fuel cells, IGT monitored the changes in anode and cathode polarizations with time. The decrease in cell performance with cell life observed with Cell DOE-2 was traced to an increase in the anode polarization, which presumably accompanied a change in the anode structure due to sintering. The cathode polarization, on the other hand, remained essentially constant with operating time of the fuel cell.

Fig. 7. Performance of Cell DOE-2 with a Ni Anode¹²⁰

Fig. 8. Performance of Cell 7-17 with a Ni Anode¹²¹

Post-test analysis of Cells DOE-2, which operated for 2000 h and 7-17, which operated for 624 h, showed conclusively that the physical characteristics of the Ni anodes changed with cell life. The results are summarized in Table 4. After 2000 h of operation, the Ni anode in Cell 7-17 decreased in porosity by 33% (complete surface area data were not available). After 624 h, the Ni anode in Cell DOE-2 showed a decrease in porosity of 15 to 45% and a decrease in surface area of 25 to 40%. Furthermore, the decrease in porosity and surface area of the anode under the solid portion of the perforated plate current collector was greater than that under the open area (or holes). Quantitative optical microscopy (QOM) measurements of Cell DOE-2 indicated that the mean pore size of the Ni anode had decreased from 13.6 to 4.7 μm , whereas mercury porosimetry of Cell 7-17 indicated that the mean pore size of the Ni anode had increased from 7.3 to 19.5 μm . The reason for the different direction of pore-size variation with sintering reported by ERC and IGT is unclear, but the different techniques used by the two organizations to measure the pore size of porous structures may be responsible. Accompanying the changes in the mean pore size and porosity of the Ni anode in Cell 7-17 was a $\sim 23\%$ shrinkage in the electrode thickness, which may be due in part to sintering and to compressive stresses applied to the cell.

Laboratory tests were conducted at GE¹²² on the sintering of porous Ni electrodes in low-BTU gas (34% H_2 /24% CO_2 /42% N_2) at 923 K. For these tests, GE measured the porosity, mean pore size, and surface area on two samples of porous Ni electrodes (one fabricated by Gould and the other by CRD) that were sintered for up to 4017 h; the results are shown in Table 5, along with data for a Ni-Cr (20 wt % Cr) electrode for comparison. For the Ni electrodes, the mean pore size increased by about 50% and the porosity decreased by 25 to 65% after 4017 h; these results are in agreement with the observations at ERC on the sintering of Ni anodes in a fuel cell test. The results on the sintering of the Ni-Cr electrode will be discussed later. Figure 9 shows the change in the porosity of the Gould and CRD porous Ni electrodes (see Table 5) with time of sintering; the plots appear to follow the relationship expressed by Eq. (16), although the slopes of the two curves are different. The change in surface area of the Gould Ni electrode with sintering is shown in Fig. 10. As shown in this figure, the change in surface area is most rapid initially, then tends towards a limiting value. By applying the analysis outlined by German¹¹⁹ for the kinetics of intermediate-state sintering, we obtained a linear plot for

Table 4. Structural Analysis of Ni Anodes Tested in Molten Carbonate Fuel Cells at 923 K

	Cell 7-17 ⁹⁴	Cell DOE-2 ⁸⁶
Operating Life, h	2000	624
Electrode thickness, mm		
Initial	0.66	0.76
Final	0.51	a
Mean Pore Size, μm		
Initial	7.3 ^b	13.6 ^c
Final	19.5 ^b	4.7 ^{c,d} , 9.6 ^{c,e}
Porosity, %		
Initial	72 ^b	80 ^c
Final	48 ^b	68 ^{c,d} , 44 ^{c,e}
Surface Area, m^2/g		
Initial	~ 0.1	0.13 ^c
Final	a	0.99 ^{c,d} , 0.076 ^{c,e}

^a Not specified.

^b Determined by mercury porosimetry.

^c Determined by quantitative optical microscopy.

^d Sample obtained from electrode under the open area (holes) of perforated plate current collector.

^e Sample obtained from electrode under the solid area of perforated plate current collector.

Fig. 9. Change in Porosity of Ni Electrodes with Sintering at 973 K in Low BTU Fuel. (Plot of data presented in Table 5 where the triangles represent the CRD sintered Ni and the circles represent the Gould sintered Ni.)

Table 5. The Physical Properties of Porous Electrodes
Heated at 923 K in Low BTU Fuel¹²²

	Time, h	Porosity, %	Mean Pore Size, μm	Surface Area, cm^2/g
Gould Sintered Ni	0	74	6.0	1120
	168	65	7.6	887
	481	61	7.8	864
	835	51	7.0	--
	1357	43	9.1	740
	2915	28	14.3	471
	3416	38	10.7	630
	4017	22	9.9	681
CRD Sintered Ni	0	65	8.3	736
	168	59	10.5	642
	1357	55	10.2	661
	2915	66	23.0	293
	3416	48	7.8	864
	4017	50	12.6	535
Sintered Ni-Cr ^a	0	52	9.6	730
	168	50	8.0	876
	481	49	7.4	947
	1357	49	7.2	979
	2915	50	6.7	1046
	4017	53	7.1	987

^a20 wt% Cr.

Fig. 10. Surface Area Change of Gould Sintered
Ni Electrode at 973 K in Low BTU Fuel¹²²

$\log (dS/S_i)/dt$ versus $\log S/S_i$ derived from the curve in Fig. 10; this plot is shown on the left-hand side of Fig. 11. The curve in Fig. 10 was also analyzed for the behavior characteristic of the initial stage of sintering (*i.e.*, linear relationship between $\log dS/dt$ and $\log t$), and a non-linear plot was obtained, which is shown on the right-hand side of Fig. 11. Thus, analysis of the data in Fig. 10 suggests that the sintering rate of Gould Ni electrode can be described by the kinetics for intermediate-stage sintering. However, due to the scatter in the experimental data in Fig. 10, the results shown in Fig. 11 must be interpreted with caution.

Fig. 11. Intermediate Stage Sintering Behavior of Gould Sintered Ni Electrode at 973 K in Low BTU Fuel. (Data obtained by analysis of Fig. 10 using the method of German.¹¹⁹)

b. Cobalt

Only limited data are available in the fuel-cell literature on the sintering of porous metals other than Ni. A fuel cell (DOE-10) that contained a Co anode was recently tested at IGT.⁸⁶ With low BTU fuel, good cell performance (850 mV at 160 mA/cm²) at 923 K was obtained for 70 h of operation (see Fig. 12). However, after 100 h the cell voltage dropped rapidly, to 770 mV, and showed very unstable performance thereafter. The erratic performance of this cell was due to large fluctuations in the anode polarization, which was attributed to structural changes to the porous Co electrode. The Co anode under the solid part of the current collector showed a decrease in surface area (0.2 to 0.066 m²/g) and porosity (71 to 36%) after 1320 h of cell operation.

Fig. 12. Performance of Cell DOE-10 with a Co Anode¹⁸⁶

c. Copper

Copper has been used as an anode,^{1,4,10,11,16} but very little information has been reported on its sintering behavior in the environment of a molten carbonate fuel cell. There are available, however, data from metallurgical studies^{113,114,123} which are useful to assess the sintering behavior of copper. From data obtained by Rhines *et al.*¹¹³ the rate of densification of Cu and Ni powders (74 to 88 μm particle size) at 1273 K in H_2 is plotted in Fig. 13 where a logarithmic form of Eq. 13 is used for the X- and Y-axes. Analysis of these data indicates that Cu powder undergoes more rapid densification than Ni powders under comparable experimental conditions at 1273 K. DeHoff *et al.*¹¹⁴ sintered samples of Cu and Ni (74 to 88 μm particle size) in dry H_2 at a temperature of 0.942 (1293 K) and 0.92 (1612 K) of their melting points, respectively. After 128 h the Cu powder sample densified to 22% void fraction; the Ni sample attained the same void fraction after a somewhat longer period--345 h. More recent studies were conducted by Shumaker and Fulrath¹²³ on the sintering of Cu and Ni particles (20 to 30 μm) at 0.8 times their respective melting points, and also showed a more rapid densification rate for Cu than that for Ni. Based on these studies, we expect that, at cell operating temperature (~ 925 K), the sintering of Cu anodes is probably more severe than that of Ni anodes. Thus, the sintering of Cu must be inhibited if it is to be practical as an anode in molten carbonate fuel cells.

The above data clearly showed that pure metals such as Ni, Co or Cu sinter much too rapidly to provide a stable porous electrode structure in operating molten carbonate fuel cells; and, therefore, the sintering of these metals must be inhibited if they are to be useful as anode materials.

Fig. 13. Densification Rates of Cu and Ni Heated at 1273 K in H₂.¹¹³ (The circles represent Ni and the triangles represent Cu.)

d. Nickel Oxide

Considerable attention has been focused on the sintering of porous metal anodes in molten carbonate fuel cells, but no data have been found on the sintering of nickel oxide cathodes. Several studies have been reported on the sintering of NiO and the effects of dopants on the sintering rate. The observations in these studies may be important in assessing the long-term physical stability of NiO cathodes.

Mass transport processes such as creep, grain boundary grooving, and sintering may be controlled by diffusional mechanisms. During sintering, vacancies or interstitial atoms may diffuse to grain boundaries and cause densification. In compounds such as oxides, it would be expected that, if diffusion processes were rate limiting during densification, the kinetics should be controlled by the slowest moving species. Furthermore, the presence of impurity dopants that alter the cation vacancy concentration should affect the sintering rates.

Data in the literature indicate that the rate of sintering for NiO powders is affected by the chemical composition of the oxide which is modified by the addition of cation dopants. Lithium-doped NiO powders were prepared from mixtures of Ni and Li salts (carbonates or nitrates) by heat treatment at 923 K by Winter,¹²⁶ at 1223 K by Tseung *et al.*,¹⁰⁵ and at 1273 K by Bielanski *et al.*,¹²⁵ and by Dry and Stone.¹²⁷ The effect

of Li-doping on the sintering rate of these four powders is illustrated in Fig. 14, where the surface area is plotted as a function of Li-dopant concentration. In each case, a maximum in the surface area of the NiO powder was observed. The wide variation of the surface-area data for the four samples reflects differences in sintering rates (the higher the maximum surface area, the lower the sintering rate). Various investigators^{105,125,127,128} believe that the different sintering rates are due to the variations in vacancy concentration which accompany doping. The small additions of Li ions fill the cation vacancies of the inherently non-stoichiometric NiO, producing a resistance to sintering. Once these vacancies are filled, Li ions enter into solid solution with the simultaneous formation of anion vacancies, which may exist only for short times, but increase the sintering rate.¹²⁷

According to Dry and Stone¹²⁷ chromium, which may be present as an impurity in NiO cathodes due to the use of stainless steel components in molten carbonate fuel cells, also has an effect on the sintering rate of NiO. Dry and Stone prepared samples of NiO doped with 1 and 5 at. % Cr by heat treatment of Ni and Cr salts at 1273 K in air for 3 h, and the surface area of the Cr-doped NiO samples was found to be ~50% that of NiO. This large decrease in surface area was attributed by the investigators to more rapid sintering due to the increase in cation vacancy concentration which Cr substitution produces.

The influence of Co additions on the sintering rate of NiO was studied by Boskovic and Stevanovic;¹²⁹ the presence of 1 and 5 at. % Co in solid solution CoO-NiO increased the rate of densification and surface-area loss during the sintering of NiO at 773 to 1173 K. This increased sintering of NiO caused by the presence of Co was explained by three factors:

- (a) A higher driving force for mass transport due to local fluctuations in stoichiometry brought about by the formation of a higher chemical potential gradient for oxygen;
- (b) A higher chemical diffusion coefficient;
- (c) A decreasing contribution of surface diffusion to the deactivation of powders during sintering.

The sintering of NiO powders in the absence of added dopants was investigated by Boskovic and Zivanovic¹³⁰ and Iida,¹³¹ who monitored the shrinkage rate of powders compacted at 9.8×10^4 kPa (1000 kg/cm²) as a function of heat treatment time and temperature. The study by Iida indicated that shrinkage due to sintering of NiO (~0.1- μ m diameter particles) did not occur at ≤ 973 K; the temperature at which shrinkage did begin was found to depend on particle size and on compacting pressure of the NiO sample. Boskovic and Zivanovic also observed that NiO compacts of low surface area (0.22 m²/g) did not exhibit shrinkage during heat treatments at ≤ 1073 K; however, NiO compacts with high surface area (24.8 and 38.4 m²/g) showed intense shrinkage beginning at 673 K. The experimental data of Boskovic and Stevanovic¹²⁹ showed that a high-surface-area (29.4 m²/g) NiO powder exhibited an increase in density (4%) and a decrease in surface area (17%) due to sintering at 773 K for 1 h.

Fig. 14. Surface Area vs Concentration of Lithium Addition in NiO Powders. [(◇), Tseung *et al.*,¹⁰⁵ (□) Bielanski *et al.*,¹²⁵ (O), Winter,¹²⁶ and (Δ), Dry and Stone.¹²⁷]

The above results on the sintering of NiO and Li-doped NiO were obtained under static experimental conditions. The NiO cathode in a molten carbonate fuel cell, on the other hand, is exposed to an environment of changing electrolyte composition, gas composition, and temperature. Consequently, the chemical composition of the cathode may change in response to fluctuations in the environment, thereby affecting the sintering of the NiO. Post-test analysis of a cathode from Cell-7-18 operated by ERC⁹³ for 1500 h at 973 K showed that the porous Ni electrode had oxidized to NiO which had a final surface area of 0.5 m²/g. However, it is not known if a decrease in surface area due to sintering had occurred. Experimental studies are desirable to ascertain if cathodes of NiO sinter in the environment of the molten carbonate fuel cell.

e. Stainless Steel

General Electric¹²² examined the sintering of porous stainless steel electrodes (Type 316) in a gas environment of 34% H₂, 24% CO₂, and 42% N₂ at 923 K. The total porosity of the electrodes appeared to be constant (~55%) for the duration of the test (4017 h); but the free porosity decreased (occluded porosity increased) to ~30% and the mean pore size decreased from 11.6 to 7.4 μm. Although the surface areas of the stainless steel electrodes were not reported, a decrease with sintering time probably accompanied the decrease in free porosity. The changes in the physical parameters observed by GE with porous stainless steel heated to 923 K suggest that this material is not a promising candidate for the anode in molten carbonate fuel cells.

3. Inhibition of Sintering in Fuel Cell Electrodes

Because porous metal electrodes of Ni and Ag readily sintered at the operating temperatures (~ 925 K) of molten carbonate fuel cells,^{29,33,40,44} researchers in the 1960's recognized that the structure of these metals must be stabilized. Various approaches were considered at that time to inhibit the sintering of porous metal electrodes. The use of ZnO ^{12,44} and CuO ⁴⁰ as additives was reported to inhibit the sintering of Ag cathodes, but these results were based on tests of short duration relative to the lifetime ($\sim 40,000$ h) presently considered for commercial cells. Furthermore, the cost of Ag is too high for commercial fuel cell electrodes. Tseung¹³² considered the use of Ag as an additive to inhibit the sintering of Ni by studying the sintering kinetics of Ni, a mixture of Ni and Ag, and Ag powders (average particle size, $3.75\text{ }\mu\text{m}$ for Ni and $3.12\text{ }\mu\text{m}$ for Ag). His study revealed that, when Ag particles were added to Ni, sintering of the mixture at 973 K was less than that of the two metals. However, it should be pointed out that the reported test period was only 24 h.

In the mid-1970's, King⁵¹ reported that proprietary anode structures were available that were physically stable in molten carbonate fuel cells for up to 7000 h; the cell performance of these stabilized anode structures and that of cells with conventional Ni electrodes is graphically displayed in Fig. 6. More recently, data published by United Technologies Corporation (UTC)¹³³ indicated near stable cell performance (see Fig. 15) in molten carbonate fuel cells for up to 13,700 h with proprietary anodes.¹³³ The rapid decay in performance after 13,700 h of cell operation was attributed to the separation of the cell components brought about by a buildup of a corrosion layer in a very localized area of the wet-seal perimeters. The cell test was terminated at 15,370 h, and mercury porosimetry was used to analyze the structure of the fuel cell anode. Figure 16 presents the relative change in the mean pore size as a function of operating time of this anode, and other anodes with shorter lifetimes, which were also reported by UTC. The data in the figure indicate that, after an initial decrease in the mean pore size, a stable pore structure was maintained with the proprietary anodes for up to 15,370 h.

Fig. 15. Performance of Cell with a Proprietary Anode¹³³

Fig. 16. Mercury Porosimetry Analysis for Relative Mean Pore Size of Proprietary Anodes after Test in Molten Carbonate Fuel Cells¹³³

The UTC study is encouraging and clearly demonstrates that aging problems associated with the sintering of anodes can be overcome. Unfortunately, owing to the proprietary nature of their study, the anode materials or the experimental conditions of the cell tests have not been made available. At present, research projects sponsored by DOE and EPRI are in progress to develop stabilized anode structures for molten carbonate fuel cells.

In the programs funded by DOE and EPRI on molten carbonate fuel cells, sintering of anodes is inhibited by the use of additives to stabilize the electrode structure. Table 6 lists the contractors that have investigated different anode materials to determine their feasibility as stabilized anode structures; the results of these investigations are reported below. In addition, at Northwestern University, Johnson^{137-140,144} is investigating the influence of dispersed refractory oxides on the sintering of Ni and undertaking studies to determine the mechanism of sintering inhibition.

a. Cobalt Additive

High surface area ($0.31 \text{ m}^2/\text{g}$) powders of Ni and Ni-10% Co were prepared and fabricated into anode structures at ERC^{94,134} for cell tests. Table 7 shows the physical properties of Ni and Ni-Co anodes before and after testing in fuel cells at 925 K. It is apparent that the electrode thickness, mean pore size, porosity, and surface area of the Ni-Co anode remain essentially unchanged after 3300 h, but these same parameters indicate that that Ni anode had sintered. The performance of the cell with a Ni anode (Cell 7-17) showed a slight decrease after about 1200 h, but no change was observed in the cell with a Ni-Co anode (Cell 110) during 3300 h of operation.

Table 6. Stabilized Anode Structures For Molten Carbonate Fuel Cells

Contractor	Electrode Material	Reference
ERC	Ni + 10% Co	94, 134
	Ni + 20% Cr	135, 136
GE	316 Stainless Steel	122
	Ni-20 wt % Cr	122
IGT	Ni + 10% alloy of Ni-20 wt % Cr	86
	Co + 10% alloy of Ni-20 wt % Cr	86
	Co + 10% Cr	86
	Co + 10% WC	86

The test results reported by ERC^{94,134} suggest that the presence of Co in the electrode structure inhibits the sintering of Ni. The mechanism of this sintering is not clearly understood but efforts to discern this mechanism have been initiated by Johnson.¹⁴¹ Some years earlier, Thummler and Thomma¹⁴² had investigated the sintering of mixtures of Co (2-4 μm) and Ni (4-6 μm) powders in H_2 at temperatures up to 1473 K using dilatometric measurements; their Ni-Co samples were compacted to 64-72% of theoretical density. Their results indicated that the Co had inhibited sintering; this effect was particularly evident when the samples were heated between 1073 and 1273 K, where homogenization is largely completed. However, the process of sintering was promoted at ≥ 1073 K until homogenization had occurred. Even though Co had inhibited the sintering of Ni, the decrease in sintering rate was relatively small. According to Hirano *et al.*¹⁴³ the volume self-diffusion coefficients of Ni and Co in the alloy are approximately the same; consequently, the rate of densification of the alloy is not expected to be much different from that of the pure metals. Although the surface diffusion coefficient for these alloys has not been measured, one would not expect the results to be greatly different from the volume diffusion results; thus surface diffusion by the presence of cobalt alone probably is insufficient to explain the results of ERC (see Table 7). Johnson¹⁴¹ suggested that the Ni-Co powders of ERC may have either been inhomogeneous (*i.e.*, not a single-phase alloy) or unintentionally contained a very beneficial impurity. To explore the various possibilities, Johnson¹⁴⁴ is investigating the sintering of high-purity, homogeneous alloy powders of Ni-Co. The results of this study will be available in the near future.

b. Chromium Additive

Table 6 lists the research groups that have examined the sintering of porous Ni and Co electrodes containing Cr. Energy Research Corp.¹³⁵ demonstrated that anodes of Ni-20% Cr did not sinter in relatively short-term tests (600 h at 973 K). This finding was substantiated by GE¹²² in their sintering experiments with Ni-20% Cr at 923 K for 4000 h in low BTU fuel (see Table 5). The results obtained by GE showed that, after heat treatment, the Ni-Cr electrode had remained virtually unchanged in

Table 7. Characterization of Nickel and Nickel-Cobalt Anodes after Operation in Molten Carbonate Fuel Cells at 925 K

	Nickel Anode ⁹⁴	Nickel-Cobalt Anode ¹³⁴
Test No.	7-17	110
Operating Life, h	2000	3300
Electrode Thickness, mm		
Initial	26	25
Final	20	24-25
Mean Pore Size, μm		
Initial	7.3	2.6
Final	19.5	2.4
Porosity, %		
Initial	72	65
Final	48	62
Surface Area, m^2/g		
Initial	~ 0.1	0.31
Final	a	0.32

^aData not reported.

porosity and dimensions, decreased slightly in mean pore size (from 9.6 to 7.1 μm), and increased somewhat in surface area (from 730 to 987 cm^2/g). The changes in the mean pore size and the surface area of the Ni-20% Cr electrode were probably due to the presence of chromium oxides.

Measurements by IGT⁸⁶ indicated that 10 wt % alloy of Ni-20% Cr is not an effective additive for inhibiting the sintering of Co and Ni anodes in molten carbonate fuel cells operated at 923 K, but that the addition of 10% Cr inhibited the sintering of Co anodes. Quantitative optical microscopy analysis was done by IGT on anodes of Co-10% Cr operated in cells for up to 3000 h at 923 K; this examination showed that the porosity and surface area remained essentially unchanged. Furthermore, fuel cells employing these anodes exhibited good, stable performance, as illustrated in Fig. 17 for Cell DOE-5. This cell showed very stable performance on both high and low BTU fuel for 3000 h, at which time the test was voluntarily terminated. The results observed by GE and IGT with electrodes of Ni-20% Cr and Co-10% Cr indicate that Cr is effective in preventing the sintering of Ni and Co during cell operation and that long-term stable performance can be obtained. However, the mechanism by which Cr inhibits the sintering of Ni and Co anodes is not clearly understood. Chromium will oxidize in the anode gas environment, and these oxides may retard the sintering of Ni and Co⁸⁶; a considerable amount of evidence has been reported in the literature^{137-141,144-147} to show that dispersed ceramic oxides can inhibit the sintering of porous metal compacts.

Fig. 17. Performance of Cell DOE-5 with a Co-10% Cr Anode⁸⁶

c. Tungsten Carbide Additive

The Institute of Gas Technology⁸⁶ examined the use of tungsten carbide (WC) as an additive to inhibit the sintering of porous Co anodes. Cells assembled with Co-10% WC anode material showed extremely poor and erratic performance because of large fluctuations in the anode polarization. These anodes appeared to have an inhomogeneous distribution of WC, which was probably due to agglomeration of WC particles during electrode fabrication. Post-test analyses of Co-10% WC anodes used in cells operated for 700 to 1200 h showed that WC did not inhibit the sintering of Co.

d. Refractory Oxides

In studies by Tikkanen *et al.*,¹⁴⁵ MgO and CaO dispersions were observed to retard the densification of Ni and Co compacts at high temperatures (~ 1525 K), where grain boundary and volume diffusion are the primary sintering mechanisms. The authors noted that the effectiveness of the oxide in retarding densification was improved by better wetting of the metal by the dispersed oxide.

In more recent studies, Johnson^{137-141,144} examined the effect of dispersed oxides on the sintering inhibition of Ni at temperatures more typical of molten-carbonate fuel cell operation (900-1000 K), where surface diffusion is the predominant sintering mechanism. Because a quantitative interpretation of the sintering of metal compacts is difficult due to the irregular geometry associated with these powders, Johnson used a sinusoidal surface of a single Ni crystal with dispersed oxides as a model system. In a parallel study, the sintering of a series of powder compacts containing the same dispersoids was also studied.

A detailed description on the kinetics of sintering of sinusoidal surfaces was presented by Johnson in several publications.¹³⁸⁻¹⁴⁰ According to this author, during sintering, the amplitude of the sinusoidal

surface is spontaneously flattened; and, if it is assumed that surface diffusion is the only transport mechanism causing a decrease in the amplitude of the sinusoid, then the amplitude decay is given by

$$\ln \frac{A}{A_0} \equiv - \frac{Bw^4 t}{1 + Na_0^4 w^2 / R_D M} \quad (24)$$

where A is the sinusoid amplitude at time, t , A_0 is the initial amplitude, w is the angular frequency of the sinusoidal surface, N is the number of particles per unit area, and a_0 is the dispersed particle radius. In addition, in Eq. 24

$$B = \gamma \Omega^2 v D_s / kT,$$

and

$$R_D = \delta D_i / (\Omega v)_s$$

where γ is the substrate surface tension, Ω is the atomic volume of the substrate, v is the area density of atoms on the substrate, D_s is the surface diffusion coefficient of the substrate, δ is the width of the region of enhanced diffusion between the substrate and the particle, D_i is the interfacial diffusion coefficient between the substrate and the particle, k is the Boltzmann's constant and T is the temperature. Finally, in Eq. 24, M is the dimensionless mobility of the particle given by

$$M \equiv \frac{kTa_0^4}{\Omega \delta D_i} \frac{u}{f} \quad (25)$$

where u is the velocity of the particle when acted upon by a force, f . Johnson¹⁴⁰ prepared sinusoidal surfaces of 5 μm wavelength ($\sim 0.8 \mu\text{m}$ amplitude) on a [100] surface of Ni crystal and studied the effect of various dispersoids on the decay rate of the sinusoidal amplitude at 1023 K in tank hydrogen. At this temperature, the amplitude decay rate of pure Ni is rapid enough that within 300 to 600 h reliable rate measurements can be obtained. Dispersions of MgO, CaO, Al_2O_3 , and Cr_2O_3 were deposited onto the single crystal surface; and these specimens were heated at 1023 K for various times up to ~ 600 h and periodically examined by interference microscopy to determine the amplitude of the sinusoids.

Figure 18 shows the normalized amplitude decay for pure Ni and Ni containing dispersoids of MgO and Al_2O_3 as a function of annealing time at 1023 K in tank hydrogen. It is evident in Fig. 18 that MgO and Al_2O_3 showed a strong influence on the amplitude decay rate of the Ni sinusoids, and also exhibited a dependence between the particle density and the amplitude decay rate which was consistent with the model. On the other hand, only a small retardation in the amplitude decay was observed with CaO; and particle growth due to Ostwald ripening and a decrease in particle density was observed.

Fig. 18. Normalized Amplitude Decay for (100) Surface, [100] Profile on 99.999 Ni Crystals at 1023 K in Tank Hydrogen.¹⁴⁰ [(○), bare Ni; (□), Al₂O₃ dispersoid ($Na_0^h = 9.9 \times 10^{-12}$ cm²); (△), MgO dispersoid ($Na_0^h = 11 \times 10^{-12}$ cm²).]

In experiments by Johnson¹⁴⁰ to study the influence of Cr₂O₃ on amplitude decay rate of Ni, the oxide disappeared from the Ni surface due to reduction and diffusion of metallic Cr into the Ni. Although Cr₂O₃ may be thermodynamically stable in tank hydrogen containing water vapor, it is not initially stable with respect to an alloy of Ni and Cr; consequently, Cr forms an alloy with Ni. Johnson calculated the minimum mole fraction of the metallic constituent in the oxide for which the oxide would not be reduced in H₂ containing 50 ppm H₂O at 1023 K, and found that for the oxides, the mole fractions are 8.4×10^{-2} for Cr₂O₃, 1.1×10^{-11} for MgO, 1.8×10^{-13} for CaO, and 4.4×10^{-14} for Al₂O₃. If a binary Ni alloy with these metals contains less than the mole fractions listed above, an oxide particle would be reduced; otherwise it would be stable. In sintering experiments with oxide dispersoids on sinusoids of Ni, Johnson found that MgO, CaO and Al₂O₃ were stable in tank H₂ at 1023 K.

Experiments¹⁴⁰ with powder compacts of Ni revealed that the surface-area loss due to sintering at 1023 K in H₂ was retarded by oxide additives (MgO, CaO, Al₂O₃, and Cr₂O₃); CaO was less effective than MgO or Al₂O₃ in retarding surface-area loss due to sintering. In the sintering experiments where Cr₂O₃ was initially present in the porous Ni compacts, it

was not certain whether or not Cr_2O_3 particles were still present on samples in tank hydrogen at 1023 K. Because of the impossibility of maintaining a dispersoid of Cr_2O_3 on a nickel substrate, Johnson¹⁴¹ concluded that stabilization of Ni by Cr cannot occur by the addition of dispersed Cr_2O_3 , therefore, an alternative explanation was sought. Johnson suggested that the Cr in an anode containing a Ni-Cr alloy oxidizes and perhaps reacts to form a stable Li-Cr oxide which, when present as dispersed particulates, may be effective in retarding Ni sintering. At the present time, experiments are under way by Johnson¹⁴⁴ to verify this hypothesis, but no definitive conclusions are available. The above experimental observations reported by Johnson indicate that surface diffusion is the primary mechanism of sintering at 1023 K and that dispersed refractory oxides are effective in retarding sintering controlled by surface diffusion.

C. Poisoning and Contamination of Electrodes

The commercialization of the molten carbonate fuel cell requires the use of coal gasification to provide the fuel. Depending on the source of the coal, various levels of contaminants may enter the fuel cell along with the fuel gas. The level of contaminant removal from the fuel gas is dictated by both economical and technical considerations, but discussion of these factors is beyond the scope of the present report. Instead, we shall discuss the effect of contaminants on the chemical and physical stability of porous electrodes in molten carbonate fuel cells. Furthermore, only sulfur and chloride containing compounds are considered since experimental data are available on these two contaminants.

1. Sulfur

Sulfur in the fuel gas can affect cell performance by two means: chemisorption onto the active sites for electrochemical reaction so that the effective surface area of the anode for oxidation is reduced; and formation of metal sulfides which change the morphology of the porous electrode and alter the balance of carbonate in the electrode/electrolyte structure. For purposes of discussion, we will be concerned primarily with the latter problem; Selman¹⁴⁸ will consider the effect of contaminants on cell performance in another DOE survey.

Sulfur compounds present in fuel gases (H_2S and COS) have a deleterious effect on the anode in molten carbonate fuel cells operating at 925 K; depending on the concentration of S, chemisorption of S or reactions to form sulfides occur. To determine the tolerance of fuel cell components to sulfur, IGT calculated the limit of stability (defined as the onset of metal sulfide formation) of various electrode materials from thermodynamic data.¹⁴⁹ For Co, Ni, Cr, and Fe, IGT calculated the limit of stability at 923 K [expressed as the $\log (\text{P}_{\text{H}_2}/\text{P}_{\text{H}_2\text{S}})$ just before sulfidation*] for a fuel gas composition range of $\log (\text{P}_{\text{CO}}/\text{P}_{\text{CO}_2})$ 0.012 to 0.673.

*The maximum concentration of H_2S that can be contacted with the metal before sulfide forms.

These results are summarized in Table 8 along with the sulfidation reactions considered in the calculation. As can be deduced from this table, the sulfur tolerance decreases in the order:

Thus, Co is more tolerant to sulfur containing gases than Ni.

Table 8. Sulfidation Reactions and Log ($P_{\text{H}_2}/P_{\text{H}_2\text{S}}$) Just Before Sulfide Formation Occurs with Various Metals at 923 K¹⁴⁸

Metal	Sulfidation Reaction ^a	log ($P_{\text{H}_2}/P_{\text{H}_2\text{S}}$)
Co	$\text{Co(s)} \rightarrow \text{Co}_9\text{S}_8\text{(s)}$	2.30
Ni	$\text{Ni(s)} \rightarrow \text{NiS(l)} \rightarrow \text{Ni}_3\text{S}_2\text{(s)}$	2.74
Cr	$\text{Cr}_2\text{O}_3\text{(s)} \rightarrow \text{Cr}_2\text{S}_3\text{(s)}$ $\text{Cr(s)} \rightarrow \text{CrS}$	-0.74 (at 1000 K) 6.02
Fe	Fe(s) $\text{Fe}_{0.747}\text{O(s)} \rightarrow \text{FeS(s)}$ $\text{Fe}_3\text{O}_4\text{(s)} \rightarrow \text{FeS(s)}$	3.22

^aSulfidation reactions assumed in gas containing a log ($P_{\text{CO}}/P_{\text{CO}_2}$) of 0.012 to 0.673.

For Ni at 923 K in the presence of H_2S ($\log P_{\text{H}_2}/P_{\text{H}_2\text{S}} < 2.74$), a liquid phase, which is an eutectic between Ni and $\text{Ni}_{3+x}\text{S}_2$ forms.¹⁵⁰ Obviously, if a large amount of liquid nickel sulfide formed at the anode in a molten carbonate fuel cell the electrode structure would be severely damaged. Eisenkolb¹⁵¹ has reported that even if only a small amount of liquid nickel sulfide (2.5 wt %, for example) were formed, liquid phase sintering may occur at 923 K; this sintering would accelerate the rate of porosity and surface area decline in the anode.

Studies funded by DOE are under way at GE and IGT to determine the effect of H_2S on cell performance. In general, the experiments involve a comparison of fuel cell performance with and without small additions of sulfur to the fuel gases. The Institute of Gas Technology¹⁴⁹ added sulfur to a fuel cell gas which consisted of simulated steam reformed naphtha fuel (52.7% H_2 , 10.4% CO_2 , 26.2% H_2O , 10.7% CO , balance inert gas) and simulated product gas from an air-blown, low-BTU coal gasification process (16% H_2 , 8.1% CO_2 , 3.4% H_2O , 19.6% CO , balance inert gas). The results of IGT showed that the addition of 10 to 20 ppm S to a cell resulted in considerable performance losses. Severe corrosion to the anode was observed after termination of the cell test, and chemical analysis revealed the presence of nickel sulfide (Ni_3S_2) in the anode. General Electric⁸⁹ examined the effect of 100 ppm H_2S on the performance of molten carbonate fuel cells operating with 34% H_2 , 24% CO_2 , and balance N_2 . The calculated ratio $\log (P_{\text{H}_2}/P_{\text{H}_2\text{S}})$ at the anode exit was 2.77 at the operating condition of the

cell (70 mA/cm^2 current density and 70% anode utilization); this value is within the thermodynamic expected region for nickel sulfide formation [$\log (P_{\text{H}_2}/P_{\text{H}_2\text{S}}) = 2.81$]. The performance of this fuel cell (CRD-016) showed a decrease, which could be traced to increased polarization ($\sim 0.5 \text{ V}$) at the anode where severe corrosion and sulfide formation was later observed. On the other hand, another cell (Cell CRD-008) operated with 100 ppm S in the fuel gas, but at 50% anode utilization [$\log (P_{\text{H}_2}/P_{\text{H}_2\text{S}}) = 3.0$ at the anode exit], showed no change in anode polarization. As was expected from the thermodynamic data, there was no evidence of sulfide formation. The above studies by GE and IGT demonstrated that nickel sulfide formation in the fuel cell occurs as predicted by thermodynamic considerations, and that cell performance is adversely affected by the presence of the sulfide in the anode.

The effect of H_2S on cell performance was investigated by UTC,¹³³ who tested the performance of small cells with 6 to 31 ppm H_2S added to the anode gas (51.0% H_2 , 10.5% CO_2 , 9.85% CO , and 28.6% H_2O). Even with as little as 6 ppm H_2S present, a significant increase ($\sim 50 \text{ mV}$) in anode polarization at 172 mA/cm^2 was reported. Further experiments are necessary to establish the maximum level of sulfur that can be tolerated at the anode without deleterious effects to performance.

The effect of sulfur on anode materials other than Ni has been investigated by IGT¹⁵² in a program funded by EPRI. For these studies, a literature search was conducted to uncover potential anode materials that are tolerant to sulfur. These specimens were immersed in a molten $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62 mol % Li_2CO_3 -38 mol % K_2CO_3) bath at 925 K with a gas environment of H_2 and CO_2 containing 270 ppm H_2S . Based on weight-change measurements after tests of up to 1000 h, the most corrosion resistant materials were found to be TiO_2 doped with Ta or Nb, Co, Ni, Cr_2O_3 with 1 mol % TiO_2 , and $\text{Mg}_{0.05}\text{La}_{0.95}\text{Cr}_2\text{O}_3$. Tests are in progress to evaluate these materials in electrochemical tests.

In a commercial molten carbonate fuel cell, part of the oxidized gases from the anode will be recycled into the cathode gas stream. Therefore, if sulfur containing compounds are present in the anode gas, sulfur will also be introduced into the cathode (as the oxides) unless provisions are made to remove it from the anode exhaust. Experiments by IGT¹⁵² showed that 35 to 43 ppm SO_2 in the oxidant (29.1% CO_2 /14.3% O_2 /3% H_2O /53.6% N_2) had very little effect on polarization of NiO cathode ($\sim 40 \text{ mV}$ at 100 mA/cm^2 current density) in cell tests of 500 h at 923 K. However, cell performance decreased by 158 mV and the anode polarization increased by 95 mV due to the transport of sulfur through the electrolyte tile and subsequent reaction with the Ni anode.

2. Chloride

The effect of chlorides on the performance of molten carbonate fuel cells is currently being investigated at GE.¹⁵³ After introducing 10 ppm HCl into the fuel gas (low BTU gas) of a cell (CRD-036) operated at 925 K for 22 days, GE found no adverse effect on performance. However, a gradual decay in performance of 200 mV was noted between day 22 and day 28 of operation. There was no evidence from post-test analysis of the cell components to indicate that the decay in cell performance could be attributed to the presence of HCl in the fuel gas.

In a subsequent cell test (CRD-049), GE¹²² added 100 ppm HCl to the anode and cathode gases by passing them through a 16 wt % HCl solution. A decrease in cell performance was observed when these gases were introduced. Measurements showed that the cathode polarization increased dramatically, but the anode polarization was unaffected. The test was terminated due to the high cathode polarization after 13 days with HCl in the gases. Post-test analysis of components from Cell CRD-049 showed that no noticeable corrosion of either the anode or wet-seal area had occurred. On the other hand, it was reported that the morphology of the nickel oxide cathode had changed and that the adherence of particles had diminished. The most severe corrosion due to the presence of HCl in the gas streams occurred with the stainless steel components (current collector, cell housings). As yet, no definite mechanism has been advanced to explain the effect of HCl on cell performance. Furthermore, the role of H₂O in accelerating the corrosive action of HCl has not been delineated.

IV. CONCLUDING REMARKS AND RECOMMENDATIONS

From an evaluation of the experimental data available in the published literature and from discussions with researchers in the fuel cell community, it would appear that a stabilized Ni anode and a Li-doped NiO cathode are the most viable electrode materials presently available for molten carbonate fuel cells. However, further research and development efforts are required before these electrodes will provide the performance that is required for commercial molten carbonate fuel cells.

In molten carbonate fuel cells, a pure metal anode will undergo a loss in surface area and a change in pore structure due to sintering; this change in the physical structure causes a decrease in cell performance. By adding inhibitors, notably metal oxides, to the porous metal structure, the sintering problem can apparently be overcome. At present, UTC has reported the longest operating cell with a stabilized anode--15370 h. From the limited data available from this test, it would appear that sintering of the anode structure was arrested. Unfortunately, data on the test conditions and the composition of the anode are proprietary. Encouraging results obtained by IGT and GE indicate that Ni-Cr and Co-Cr electrodes are structurally stable at the typical operating temperature (925 K); however, these results were obtained in tests of only 4000 h or less. Preliminary results obtained at ERC suggested that Co inhibited the sintering of Ni in molten carbonate fuel cells, but other studies indicated that Co is not an adequate inhibitor.

Corrosion and electrochemical oxidation of anodes containing Ni does not appear to be a problem, provided that the anode polarization does not exceed about 200 mV. However, experimental studies indicate that the presence of sulfur containing compounds, which may be present as a contaminant in the fuel gas, have a deleterious effect on Ni anode stability and performance. At 925 K, sulfur reacts with nickel metal to form a liquid phase which damages the electrode structure. Other contaminants, such as the halides, may also be deleterious to electrode stability and performance, but the effects of these impurities have only recently been studied.

Even with the reported success on inhibiting the sintering of anodes in operating fuel cells, there still remains a great need for further research and development studies before an anode suitable for commercialization will be available. The following areas of research on anode development are suggested:

1. Verification. Long-term tests (>10,000 h) of stabilized anodes operating at realistic conditions in molten carbonate fuel cells are required to substantiate the results obtained from sintering studies of shorter duration.
2. Optimization. The optimum amount of Cr or alternate additive required to inhibit the sintering of anodes should be determined.
3. Cost Selection. Data are required to determine whether the advantages of Co-Cr anodes over Ni-Cr anodes outweigh the higher cost of Co.
4. Alternative Electrode Material. Additives to inhibit sintering of a low cost anode material such as Cu should be explored.
5. Mechanistic Studies. The mechanism(s) by which additives inhibit sintering in anodes should continue to be investigated.
6. Chemical Stability. The stability of the additives in molten carbonates should be evaluated to determine their long-term stability as a sintering inhibitor.
7. Contaminant Effects. The maximum levels and the long-term effects of fuel contaminants on the stability (physical and chemical) of electrodes and sintering inhibitors should be determined in realistic operating conditions.
8. Fuel Cell Operating Conditions. The effects of cell temperature, gas pressure, and gas composition on the aging of anodes should be determined. (These studies require post-test analyses of anodes from fuel cells operated under realistic conditions and in controlled laboratory experiments.)

The following points are not directly related to the problem of anode aging in molten carbonate fuel cells, but are important for the success of the molten carbonate technology: maintaining adequate electrode dimensional tolerance during fabrication, cost and availability of materials for anodes, and verification of electrolyte storage in anode structure. These three points, which were mentioned by researchers in the DOE-funded program as possible obstacles to the development of a commercial fuel cell, must be addressed.

In the last decade there has been considerable effort in molten carbonate fuel cell technology devoted to studying Ni and other metals for anodes, but very little attention has been focused on cathodes. It is generally conceded that NiO is the prime candidate for the cathode; however, the NiO cathode in its present form has many shortcomings.

The state-of-the-art NiO cathode is generally formed by *in situ* oxidation of porous Ni electrodes. In general, the porous Ni electrodes used as anodes and cathodes have only minor differences in their initial physical parameters, in particular, the electrode is thinner and the mean pore size is larger for the cathode. However, after oxidation *in situ* of the NiO cathode, the mean pore size and electrode thickness are different from the initial values. Furthermore, the cathode structure is mechanically weak, and the NiO is an insulator which must be doped with Li_2O from the electrolyte to provide reasonable electronic conductivity. To overcome the shortcomings inherent in the state-of-the-art cathode, research in the following areas is suggested:

1. Cathode Fabrication. Alternative methods to form the NiO cathode structure should be investigated. In particular, methods to control the physical parameters of NiO cathodes prior to cell assembly should be considered.
2. Physical Strength. Cell design changes may require greater strength for the cathode. Thus, methods to improve the physical strength of cathodes should be explored.
3. Electrical Conductivity. Experiments to measure and enhance the conductivity of the NiO cathode should be pursued; and the effect of corrosion or oxidation products (for example, Cr from stainless steel cell components) on the electrical conductivity of NiO should be examined in more detail. Furthermore, measurements should be made to determine if changes occur in the electrical conductivity of Li-doped NiO cathodes with cell aging.
4. NiO Stability. Long-term cell tests under realistic operating conditions are required to evaluate the structural (sintering) and chemical (corrosion) stability of NiO in molten carbonates.
5. Alternative Cathode. Research on alternative cathode materials with higher electrical conductivity and greater physical strength than those of NiO should be considered.
6. Contaminant Effects. The maximum levels and the long-term effects of contaminants, which are introduced with the oxidant, on the stability (physical and chemical) of electrodes tested under realistic operating conditions

should be determined. In particular, information on the effects of contaminants on the stoichiometry, electronic conductivity, and physical strength of NiO cathodes is desirable.

7. Fuel Cell Operating Conditions. The effects of cell temperature, gas pressure, and gas composition on the physical and chemical stability of NiO cathodes should be determined by testing cathodes in fuel cells operated under realistic conditions and in controlled laboratory experiments.

Analysis of the published literature and discussions with researchers indicate that there are numerous problem areas related to electrode aging and degradation in molten carbonate fuel cells. Solutions to the problem areas discussed above would provide some advancement in the technology which is required for commercialization of molten carbonate fuel cells.

ACKNOWLEDGMENT

The author would like to express his appreciation to the organizations and individuals listed below for their contributions to this report: Argonne National Laboratory, J. P. Ackerman; Electric Power Research Institute, J. Appleby; Energy Research Corporation, D. Dharja and H. Maru; General Electric Company, R. Arendt, M. Breiter, K. Browall, N. Choudhury, A. Fragala, J. Harrison, C. Iacovangelo, J. McElroy, and J. Weininger; Institute of Gas Technology, L. Marianowski; Northwestern University, D. L. Johnson; United Technologies Corporation, L. Bregoli, B. Houghtby, H. Kunz, S. Szymanski, and W. Vogel.

The author would like to acknowledge the cooperation of L. Marianowski for providing numerous references quoted in Section II, J. Frazier (ANL) for his literature search on the molten carbonate fuel cell technology, and R. D. Pierce (ANL) and J. Harmon (ANL) for their review of the manuscript.

REFERENCES

1. G. H. Broers, *High Temperature Galvanic Fuel Cells*, Ph.D. Thesis, University of Amsterdam, 1958.
2. E. Gorin and H. L. Recht, Chem. Eng. Prog. 55(8), 51 (1959); *Fuel Cells*, ed. by W. Mitchell, Academic Press, New York, NY, 1963, p. 193.
3. W. Vielstich, *Fuel Cell: Modern Processes for the Electrochemical Production of Energy*, Wiley-Interscience, London, 1965, p. 20.
4. G. H. J. Broers and J. A. A. Ketelaar, *Fuel Cells*, ed., G. J. Young, Reinhold, New York, NY, 1960, p. 78 and Ind. Eng. Chem. 52, 303 (1960).
5. E. Baur, W. D. Treadwell, and G. Trumpler, Z. Elektrochem. 27, 199 (1921).

6. O. K. Davtyan, Bull. Acad. Sci. U.S.S.R., Classe Sci. Tech. 1, 107 (1946); 2, 215 (1946).
7. J. P. Ackerman, *Proceedings of the Symposium on Electrode Materials for Energy Conversion and Storage*, ed., J. D. E. McIntyre, S. Srinivasan, and F. G. Will, The Electrochemical Society, Princeton, NJ, p. 634 (1977).
8. Institute of Gas Technology Project 8984 Quarterly Status Report for the Period July 1 through September 30, 1976, *Fuel Cell Research on Second Generation Molten-Carbonate Systems, Volume II, Characteristics of Carbonate Melts*, Institute of Gas Technology, Chicago, IL.
9. G. H. J. Broers, *Fuel Cells*, prepared by Editors of Chemical Engineering Progress, A.I.Ch.E., New York, NY, 1963, p. 90.
10. G. H. J. Broers, M. Schenke, and C. G. Piepers, *Advanced Energy Conversion*, 4, 131 (1964).
11. G. H. J. Broers and M. Schenke, *Fuel Cells, Volume II*, ed., G. J. Young, Reinhold, New York, NY, p. 6 (1963).
12. H. H. Chambers and A. D. S. Tantram, *Ind. Eng. Chem.* 52, 295 (1960).
13. H. H. Chambers and A. D. S. Tantram, *Fuel Cells*, ed., G. J. Young, Reinhold, New York, NY, p. 94 (1960).
14. A. N. Webb, W. B. Mather, and R. M. Suggitt, *J. Electrochem. Soc.* 112, 1059 (1965).
15. I. Trachtenberg, *Fuel Cell Systems*, *Advances in Chemistry Series 47*, ed., R. F. Gould, American Chemical Society, Washington, DC, p. 232 (1965).
16. N. Sakikawa and N. Kamiya, *Electroanal. Abstr.* 6, 1970 (1968).
17. D. R. Warren, *Mech. Chem. Eng. Trans.* 3, 81 (1967).
18. A. C. C. Tsueng, *J. Appl. Electrochem.* 2, 137 (1972).
19. P. K. David and F. Krajcsovics, *Power Sources 4*, ed., D. H. Collins, Oriel Press, Newcastle upon Tyne, England, p. 595 (1973).
20. E. A. Dezubay, Conference Preprint No. 150-E, Presented at the Society of Automotive Engineers, Aeronautics Meeting, New York, NY, April, 1960.
21. D. L. Douglas, *Ind. Eng. Chem.* 52, 308 (1960); *Fuel Cells*, ed., G. J. Young, Reinhold, New York, NY, p. 129 (1960).
22. Y. L. Sandler, *J. Electrochem. Soc.* 109, 1115 (1962).
23. E. B. Shultz, K. S. Vorres, L. G. Marianowski, and H. R. Linden, *Fuel Cells, Volume II*, ed., G. J. Young, Reinhold, New York, NY, p. 24 (1963).

24. L. G. Marianowski, J. Meek, E. B. Schultz, and B. S. Baker, *Proceedings 17th Power Sources Conference*, P.S.C. Publications Committee, Red Bank, NJ, p. 72 (1963).
25. I. Trachtenberg, *J. Electrochem. Soc.* **111**, 110 (1964).
26. K. Ito and T. Takahashi, *J. Electrochem. Soc. Japan* **32**, 176 (1964); **33**, 62 (1965); **33**, 194 (1965).
27. R. L. Moss and H. R. Gibbens, *Cobalt*, 115 (Sept. 1965).
28. J. K. Truitt and F. L. Gray, *Proceedings 19th Power Sources Conference*, P.S.C. Publications Committee, Red Bank, NJ, p. 49 (1965).
29. G. H. J. Broers and M. Schenke, *Hydrocarbon Fuel Cell Technology*, ed., B. S. Baker, Academic Press, New York, NY, p. 225 (1965).
30. G. H. J. Broers and M. Schenke, *Rev. Energ. Primarie* **1**, 54 (1965).
31. A. D. S. Tantram, A. C. C. Tseung, and B. S. Harris, *Hydrocarbon Fuel Cell Technology*, ed., B. S. Baker, Academic Press, New York, NY, p. 187 (1965).
32. A. Salvadori, *Hydrocarbon Fuel Cell Technology*, ed., B. S. Baker, Academic Press, New York, NY, p. 267 (1965).
33. I. Trachtenberg, *Hydrocarbon Fuel Cell Technology*, ed., B. S. Baker, Academic Press, New York, NY, p. 251 (1965).
34. J. Millet and R. Buvet, *Rev. Energ. Primaire* **1**, 49 (1965); *Hydrocarbon Fuel Cell Technology*, ed., B. S. Baker, Academic Press, New York, NY, p. 285 (1965).
35. G. K. Stepanov and A. M. Trunov, *Electrochemistry of Molten and Solid Electrolytes*, Vol. 3, ed., A. N. Baraboshkin, Consultants Bureau, New York, NY, p. 73 (1965).
36. E. S. Argano, T. Schmidt, and D. T. Wasan, *Chem. Eng. Progress Symposium Series No. 77*, **63**, 26, (1967).
37. B. S. Baker, *Proceedings 21st Power Sources Conference*, P. S. C. Publications Committee, Red Bank, NJ, p. 26 (1967).
38. F. L. Gray, *Proceedings 21st Power Sources Conference*, P. S. C. Publications Committee, Red Bank, NJ, p. 26 (1967); *Deuxiemes Journees Internationales d'Etude des Piles a Combustible*, Proceedings of conference held under the joint sponsorship of SERAI and COMASCI, Brussels, June 19-23, 1967, p. 385.
39. A. Clauss and G. Genin, *Deuxiemes Journees Internationales d'Etude des Piles a Combustible*, Proceedings of conference held under joint sponsorship of SERAI and COMASCI, Brussels, June 19-23, 1967, p. 340.

40. A. Salvadori, M. Louichon, and c. Lebvas, *Deuxiemes Journees Internationales d'Etude des Piles a Combustible*, Proceedings of conference held under joint sponsorship of SERAI and COMASCI, Brussels, June 19-23, 1967, p. 392.
41. K. Shiota, H. Tamura, and T. Ishino, Chem. Abstr. 67, 78357Z (1967).
42. T. Takahashi, S. Nakamura, and K. Ito, *Internationales Symposium Brennstoffelemente*, ed., K. Schwabe and E. Winkler, Akademie-Verlag, Berlin, 1968, p. 327.
43. H. E. Huynink, Energy Conv. 12, 131 (1972).
44. A. C. C. Tseung and A. D. S. Tantram, *Science of Ceramics*, Vol. 4, ed., G. H. Stewart, British Ceramic Society, Stokes-on-Kent, 1968, p. 367.
45. B. S. Baker, L. G. Marianowski, J. Zimmer, and G. Price, *Hydrocarbon Fuel Cell Technology*, ed., B. S. Baker, Academic Press, New York, NY, 1965, p. 293.
46. L. G. Marianowski, *JP-4 Fueled Molten Carbonate Fuel Cells*, IGT Project No. S-901, U. S. Army Contract No. DA-44-009-AMC-1456 (T) Jan. 1, 1966 to Nov. 15, 1967, Institute of Gas Technology, Chicago, IL.
47. M. Schenke and G. H. J. Broers, *Power Sources 1966*, ed., D. H. Collins, Pergamon, Oxford, England, 1967, p. 459.
48. M. Schenke and G. H. J. Broers, *Deuxiemes Journees Internationales d'Etude des Piles a Combustible*, Proceedings of conference held under joint sponsorship of SERAI and COMASCI, Brussels, June 19-23, 1967, p. 398.
49. E. S. Argano and J. Levitan, J. Electrochem. Soc. 116, 153 (1969).
50. G. G. Arkhipov and G. K. Stepanov, *Electrochemistry of Molten and Solid Electrolytes, Volume 3*, ed., A. N. Baraboshkin, Consultants Bureau, New York, NY, 1965, p. 67.
51. J. M. King, *Proceedings 10th Intersociety Energy Conversion and Engineering Conference*, Newark, DE, Aug. 18-22, 1975, p. 1.
52. M. L. Kronenberg, J. Electrochem. Soc. 109, 753 (1962).
53. T. Takahashi, J. Electrochem. Soc. Japan 34, 60 (1966).
54. L. G. Marianowski, private communication, February 1979.
55. L. G. Austin, *Fuel Cells, A Review of Government-Sponsored Research, 1950-1964*, NASA-SP-120, National Aeronautics and Space Administration, Washington, DC, 1967, p. 68.
56. *Ibid.*, p. 120.

57. *Ibid.*, p. 119.
58. L. P. Klevtsov, G. G. Arkhipov, and G. K. Stepanov, *Elektrokhimiya* 1, 1304 (1965).
59. L. P. Klevtsov, G. G. Arkhipov, and G. K. Stepanov, *Elektrokhimiya* 3, 888 (1967).
60. A. V. Silakov, G. S. Tyurikov, and N. P. Vasilistov, *Elektrokhimiya* 1, 613 (1965); 2, 205 (1966).
61. M. A. Volgin and A. L. L'vov, *Elektrokhimiya* 7, 1388 (1971); 7, 1562 (1971).
62. G. S. Tyurikov, N. P. Vasilistov, A. V. Silakov, and Y. M. Pashkov, *Elektrokhimiya* 5, 309 (1969).
63. Y. M. Pashkov and G. S. Tyurikov, *Elektrokhimiya* 5, 1112 (1969).
64. Y. M. Pashkov and G. S. Tyurikov, *Elektrokhimiya* 3, 441, (1967).
65. S. Chudoba and Z. Kubas, *High Temp. Sci.*, 8, 377 (1976).
66. *Ibid.*, p. 385.
67. S. B. Meibuhr, *Electrochim. Acta* 11, 1301 (1966).
68. R. P. Tischer, *Electrochim. Acta* 11, 1309 (1966).
69. S. B. Meibuhr, *Electrochim. Acta* 11, 1325 (1966).
70. L. F. Martin, *Storage Batteries and Rechargeable Cell Technology*, Noyes Data Corporation, Park Ridge, NJ, 1974.
71. M. W. Ranney, *Fuel Cells, Recent Developments*, Noyes Development Corporation, Park Ridge, NJ, 1969.
72. *Fuel Cells*, patent review compiled by the research staff of the Technical and Economical Publishing Company, The Hague, Netherlands, 1969.
73. M. D. Ingram and G. J. Janz, *Electrochim. Acta* 10, 783 (1965).
74. M. Pourbaix, *Thermodynamics of Dilute Solutions*, Arnold, London, England, 1949.
75. F. Klein, *Les Piles a Gas de Haute Temperature: Electrolyte de Carbonates Alcalins Fondus*, Ph.D. Thesis, University of Nancy, France, 1971.
76. P. Degobert and O. Bloch, *Bull. Soc. Chim. Fr.*, 1887 (1962).
77. H. J. Davis and D. R. Kinnibrugh, *J. Electrochem. Soc.* 117, 392 (1970).

78. G. J. Janz, A. Conte, and E. Neuenschwander, *Corrosion* **19**, 292t (1963).
79. G. J. Janz and A. Conte, *Corrosion* **20**, 237t (1964).
80. G. J. Janz and A. Conte, *Electrochim. Acta* **9**, 1269 (1964).
81. H. E. Bartlett and K. E. Johnson, *J. Electrochem. Soc.* **114**, 457 (1967).
82. J. Dubois, *Ann. Chim.* **10**, 145 (1965).
83. I. Trachtenberg and D. F. Cole, *Fuel Cell Systems-II*, Advances in Chemistry Series 90, ed., R. F. Gould, American Chemical Society, Washington, DC, 1969, p. 269.
84. K. E. Johnson, *High Temperature Technology*, Proceedings of the Third International Symposium on High Temperature Technology held at Asilomar in Pacific Grove, CA, September 17-20, 1967, Butterworths, London, 1968, p. 493.
85. P. Drossbach and D. Sauermann, *Electrochim. Acta* **9**, 1373 (1964).
86. Institute of Gas Technology, Project 9105 Annual Status Report for 1978, *Fuel Cell Research on Second-Generation Molten Carbonate Systems*, Institute of Gas Technology, Chicago, IL.
87. G. J. Janz and A. Conte, *Electrochim. Acta* **9**, 1279 (1964).
88. L. F. Grantham and P. B. Ferry, *Proceedings of the International Symposium on Molten Salts*, ed., J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, and N. E. Richards, The Electrochemical Society, Inc. Princeton, NJ, 1976, p. 270.
89. General Electric Company, Quarterly Progress Report, May 15, 1978 through August 15, 1978, *Development of Molten Carbonate Fuel Cells for Power Generation*, SRD-78-148, General Electric Company, Corporate Research and Development, Schenectady, NY, September, 1978.
90. F. T. Bacon, *Fuel Cells*, ed., G. J. Young, Reinhold, New York, NY, 1960, p. 51.
91. J. P. Ackerman *et al.*, *Advanced Fuel Cell Development, Progress Report for January-March 1977*, Argonne National Laboratory Report ANL-77-29 (June 1977).
92. H. C. Maru and L. G. Marianowski, *Extended Abstracts*, Vol. 76-2, The Electrochemical Society, Inc., Princeton, NJ, p. 82 (1976).
93. Energy Research Corporation, *Technical Progress Report for the Period April-June, 1978, High Temperature Molten Carbonate Fuel Cells*, SAN/1196-9, Energy Research Corporation, Danbury, CT (Sept. 1978).
94. Energy Research Corporation, *Technical Progress Report for the Period July-September, 1978, High Temperature Molten Carbonate Fuel Cells*, SAN/1196-10, Energy Research Corporation, Danbury, CT (Nov. 1978).

95. R. J. Moore and J. White, *J. Mat. Sci.* **9**, 1393 (1974).
96. *Ibid.*, p. 1401.
97. Oak Ridge National Laboratory, *Molten Carbonate Fuel Cell Program*, ORNL/TM-6168/V3, Oak Ridge National Laboratory, Oak Ridge, TN, (Sept. 1978).
98. M. C. Pope and N. Birks, *Corr. Sci.* **17**, 747 (1977).
99. W. D. Johnston, *J. Chem. Educ.* **36**, 605 (1959).
100. S. Van Houten, *J. Phys. Chem. Solids* **17**, 7 (1960).
101. J. B. Goodenough, D. G. Wickham, and W. J. Croft, *J. Phys. Chem. Solids* **5**, 107 (1958).
102. A. J. Bosman and C. Crevecoeur, *Phys. Rev.* **144**, 763 (1966).
103. S. P. Mitoff, *J. Chem. Phys.* **35**, 882 (1961).
104. S. Pizzini and R. Morlotti, *J. Electrochem. Soc.* **114**, 1179, (1967).
105. A. C. C. Tseung, B. S. Hobbs, and A. D. S. Tantram, *Electrochim. Acta* **15**, 473, (1970).
106. B. K. Andersen, *Thermodynamic Properties of Molten Alkali Carbonates*, Ph.D. Thesis, The Technical University of Denmark, 1975.
107. R. Cohen-Adad, M. Michaud, J. Said, and A. P. Rollet, *Bull. Soc. Chim. Fr.* 356 (1961).
108. E. G. Bunzel and E. J. Kohlmeyer, *Z. Anorg. Chem.* **254**, 1 (1947).
109. L. F. Grantham and P. B. Ferry, *Extended Abstracts*, Vol. 76-1, The Electrochemical Society, Inc. Princeton, NJ, p. 970 (1976).
110. G. C. Kuczynski, *Powder Metallurgy*, ed., W. Leszynski, Interscience, New York, NY, p. 11 (1961).
111. F. Thummler and W. Thomma, *Metal. Rev.* **12**, 69 (1967).
112. A. J. Schaler, *Trans. A.I.M.E.* **185**, 796 (1949).
113. F. N. Rhines, R. T. DeHoff, and R. A. Rummel, *Agglomeration*, ed., W. A. Knepper, Interscience, New York, NY, p. 351 (1962).
114. R. T. DeHoff, R. A. Rummel, H. P. LaBuff, and F. N. Rhines, *Modern Developments in Powder Metallurgy, Volume 1*, ed., H. H. Hausner, Plenum Press, New York, NY, p. 310 (1966).
115. R. T. DeHoff, R. A. Rummel, and F. N. Rhines, *Powder Metallurgy*, ed., W. Leszynski, Interscience, New York, NY, p. 31 (1961).

116. R. M. German and Z. A. Munir, *J. Amer. Ceram. Soc.* **59**, 379 (1976).
117. R. M. German and Z. A. Munir, *Sintering and Catalysis* (Materials Science Research, Vol. 10), ed., G. C. Kuczynski, Plenum Press, New York, NY, p. 249 (1975).
118. R. M. German and Z. A. Munir, *Sintering and Catalysis* (Materials Science Research Vol. 10), ed., G. C. Kuczynski, Plenum Press, New York, NY, p. 259 (1975).
119. R. M. German, *J. Amer. Ceram. Soc.* **61**, 272 (1978).
120. Institute of Gas Technology, Project 9105 Quarterly Technical Progress Report for the Period January 1 through March 31, 1978, *Fuel Cell Research on Second-Generation Molten-Carbonate Systems*, Institute of Gas Technology, Chicago, IL, July, 1978.
121. Energy Research Corporation, Technical Progress Report for the Period January-March, 1978, *High Temperature Molten Carbonate Fuel Cells*, SAN/1196-8, Energy Research Corporation, Danbury, CT, May, 1978.
122. General Electric Company, Quarterly Progress Report, November 15, 1978 through February 15, 1979, *Development of Molten Carbonate Fuel Cells for Power Generation*, General Electric Company, Schenectady, NY, March, 1979.
123. C. B. Shumaker and R. M. Fulrath, *Sintering and Related Phenomena*, (Materials Science Research, Vol. 6), ed., G. C. Kuczynski, Plenum Press, New York, NY, p. 191 (1973).
124. A. Bielanski, J. Deren, J. Haber, and J. Sloczynski, *Trans. Farad. Soc.* **58**, 166 (1962).
125. A. Bielanski, K. Dyrek, Z. Kluz, J. Sloczynski, and T. Tobiasz, *Bull. Acad. Pol. Sci.* **12**, 657 (1964).
126. E. R. S. Winter, *Disc. Farad. Soc.* **28**, 183 (1959).
127. M. E. Dry and F. S. Stone, *Disc. Farad. Soc.* **28**, 192 (1959).
128. M. R. Notis, P. A. Urlick, and R. M. Spriggs, *Sintering and Related Phenomena* (Materials Science Research, Vol. 6), ed., G. C. Kuczynski, Plenum Press, New York, NY, p. 409 (1973).
129. S. B. Boskovic and M. Stevanovic, *J. Mat. Sci.* **10**, 25 (1975).
130. S. B. Boskovic and B. M. Zivanovic, *J. Mat. Sci.* **9**, 117 (1974).
131. Y. Iida, *J. Amer. Ceram. Soc.* **41**, 397 (1958).
132. A. C. C. Tseung, *J. Appl. Electrochem.* **1**, 279 (1971).

133. United Technologies Corporation, Annual Report, December, 1978, *Advanced Technology Fuel Cell Program*, Project RP114-2, EPRI Report Number EM-956.
134. D. Dharia, D. Kinnibrugh, P. Patel, and A. Pigeaud, paper presented at the Molten Carbonate Fuel Cell Workshop, Oak Ridge, TN, Oct. 31 to Nov. 2, 1978.
135. Energy Research Corporation, Third Quarter Technical Progress Report, E-3-3, *High Temperature Molten Carbonate Fuel Cells*, Energy Research Corporation, Danbury, CT, December, 1976.
136. Energy Research Corporation, Fifth Quarter Technical Progress Report E-3-5, *High Temperature Molten Carbonate Fuel Cells*, Energy Research Corporation, Danbury, CT, July, 1977.
137. D. L. Johnson, *Script. Met.* 8, 905 (1974).
138. D. L. Johnson, *Sintering and Catalysis* (Materials Science Research, Vol. 10), ed., G. C. Kuczynski, Plenum Press, New York, NY, p. 133 (1975).
139. D. L. Johnson, *J. Mat. Sci.*, 11, 2312 (1976).
140. D. L. Johnson, *Influence of Dispersed Refractory Oxides in Retarding Catalyst Sintering*, Contract No. RP-371-1, Interim Report, sponsored by Electric Power Research Institute, Inc. (March 1978).
141. D. L. Johnson, *Influence of Dispersed Refractory Oxides in Retarding Catalyst Sintering*, Quarterly Report, August 1 to October 31, 1978, Contract No. RP-371-1-3, sponsored by Electric Power Research Institute, Inc. (Nov. 1978).
142. F. Thummler and W. Thomma, *Modern Developments in Powder Metallurgy* (Fundamentals and Methods, Vol. 1), ed., H. H. Hausner, Plenum Press, New York, NY, p. 361 (1966).
143. K. J. Hirano, R. P. Agarwalla, B. L. Averbach, and M. Cohen, *J. Appl. Phys.* 33, 3049 (1962).
144. D. L. Johnson, *Influence of Dispersed Refractory Oxides in Retarding Catalyst Sintering*, Quarterly Report, November 1, 1978 to January 31, 1979, Contract No. RP-371-1-3, sponsored by Electric Power Research Institute (Feb. 1979).
145. M. H. Tikkanen, B. O. Rosell, and O. Wiberg, *Powder Met.* No. 10, 49 (1962).
146. G. C. Kuczynski and H. W. Lavendel, *Internat. J. Powder Met.*, 5, 19 (1969).
147. J. Brett and L. Seigle, *Acta Met.* 14, 575 (1966).

148. J. R. Selman, *Molten Carbonate Fuel Cell Performance*, to be published.
149. Institute of Gas Technology, Project 8894 Final Status Report for the Period of July 1, 1976 through September 30, 1977, *Fuel Cell Research on Second Generation Molten Carbonate Systems, Volume I, Cell Performance as a Function of Feed-Gas Quality*, Institute of Gas Technology, Chicago, IL.
150. T. Rosenquist, J. Iron Steel Inst. 176 (1954) 37.
151. F. Eisenkolb, *Powder Metallurgy*, ed., W. Leszynski, Interscience, New York, NY, p. 75 (1961).
152. Institute of Gas Technology, *Development of Sulfur-Tolerant Components for Second Generation Molten Carbonate Fuel Cells*, Interim Report April 1979, Research Project 1085-2 Sponsored by Electric Power Research Institute, Institute of Gas Technology, Chicago, IL.
153. General Electric Co., *Development of Molten Carbonate Fuel Cells for Power Generation*, Progress Report August 15, 1978 through November 15, 1978, Schenectady, NY, December 1978.