

Control of Corrosion in Molten Carbonate Fuel Cells

THE APPLICATION OF PLATINUM GROUP METALS IN ANODE COMPONENTS

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Molten carbonate fuel cells have the potential to succeed phosphoric acid fuel cells as systems for large scale electrical power generation. Their introduction, however, will depend on the wide acceptance of first generation phosphoric acid technology and on solutions being found to a number of significant technical problems, including corrosion of fuel cell components by the molten carbonate electrolyte. Ruthenium, rhodium, palladium, platinum, silver and gold have all been shown to exhibit resistance to corrosion by molten carbonates under the conditions experienced at the anode of a molten carbonate fuel cell. In addition, rhodium and ruthenium are not wetted significantly by the molten carbonate electrolyte.

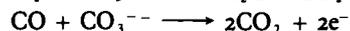
Fuel cells offer a very attractive means of converting the chemical energy of a fuel and an oxidant to electrical energy, since the conversion efficiency is not subject to the limitation of the Carnot cycle. Phosphoric acid fuel cell technology is accepted as being nearest to commercialisation for large scale electric power generation. Dozens of prototype stationary phosphoric acid fuel cell units have been demonstrated at electric utilities and by users of co-generated heat and power in the United States of America and Japan. While these were generally successful they were considered to be too costly for commercial use. A large, 60 to 80,000 MW fuel cell market can be envisaged for the period 1996 to 2010, based on mature market prices (1). However, near term prices of £1450 to £1750/kW for fuel cell power plants are well above the mature market price of £350 to £600/kW. A significant volume of production, say 2,000 to 3,000 MW, at lower prices will be required to support the introduction of phosphoric acid fuel cell units over the next 10 to 15 years (2).

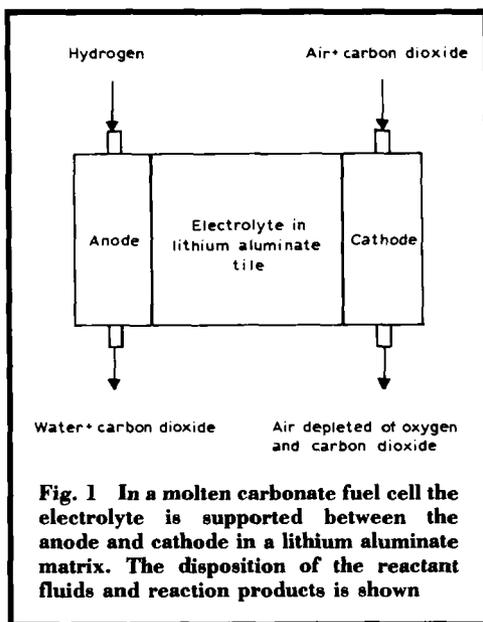
For the future, molten carbonate fuel cells

are particularly attractive since the operating temperature is generally about 650°C and the reaction kinetics are significantly faster than in lower temperature cells. In addition, the ohmic resistance of the usual 62 : 38 mol per cent lithium carbonate : potassium carbonate electrolyte is relatively low, while efficiencies of the order of 50 to 55 per cent have been reported (3).

A schematic diagram of a molten carbonate fuel cell is shown in Figure 1. The electrolyte is supported in a matrix of lithium aluminate which is termed a "tile". The separator plate and current collector are generally made from stainless steel. A practical fuel cell consists of repeated layers of electrolyte "tile", cathode, bipolar plate and anode, see Figure 2.

The carbonate ion takes part in the electrode reactions, and the composition of the melt remains constant due to a continuous transfer of carbonate ions from the cathode to anode.





During early work on molten carbonate fuel cells platinum, palladium and palladium-silver alloys were used as anode materials (4) but they were rejected on the grounds of cost. At present, nickel or nickel-chromium is used for the anode in state-of-the-art cells, while the cathode is generally made of nickel oxide. However, the cathodes in particular are subject to corrosion problems.

Corrosion

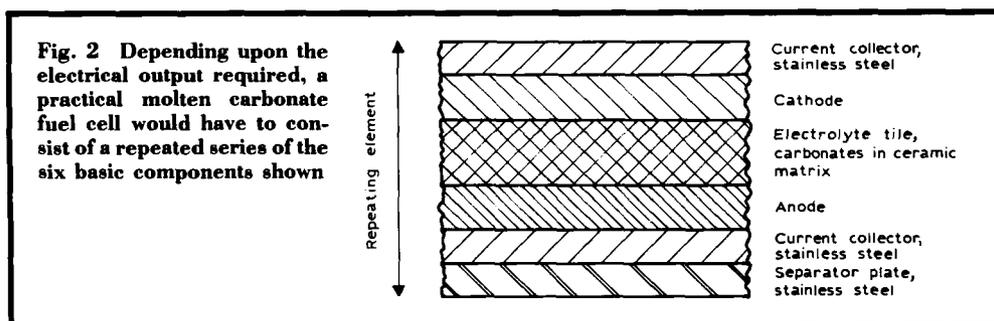
Molten carbonate is a very aggressive medium and the corrosion of fuel cell components poses significant problems. The resistance of any material to corrosion by

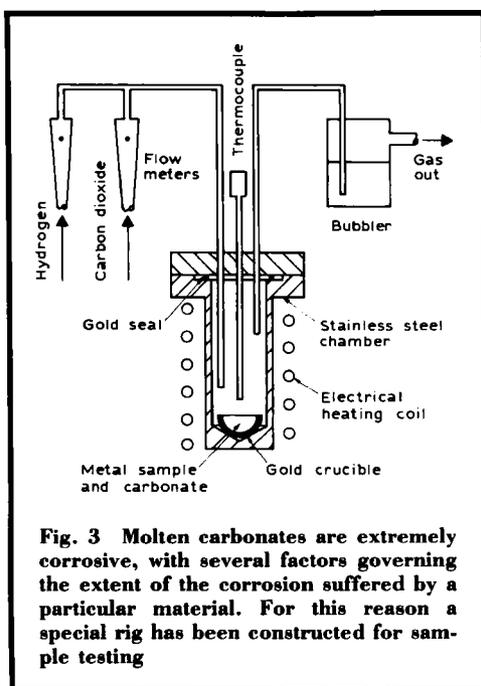
molten carbonate is dependent on a large number of factors (5), including moisture and impurities content, temperature, and the gas atmosphere above the melt. Another important factor affecting corrosion is the wettability of the materials by molten carbonate, and many materials are completely smothered by molten alkali carbonate. Since there are so many factors governing corrosion and wetting resistance it is not surprising that the literature in this field appears confusing. Differences in test procedures, purity of melts, gas atmospheres and temperatures, for example, can all give widely differing results.

The present work has shown that ruthenium, rhodium, palladium, platinum, silver and gold show promise as corrosion resistant materials for use at the anode in molten carbonate fuel cells. A series of static corrosion tests has been carried out on these metals using a specially designed rig which allowed the simultaneous testing of 6 samples. A schematic diagram of a single test chamber is shown in Figure 3, on the following page.

Preliminary tests demonstrated that gold did not dissolve in molten carbonate, so all subsequent corrosion tests were carried out in gold crucibles. A typical test involved placing a metal foil sample (2 × 1 cm) and the carbonates (0.5 g) inside a small gold crucible which was then maintained inside the test chamber at a temperature of 650°C, under a specified gas atmosphere.

A typical mixed carbonate electrolyte was prepared from lithium and potassium carbonates which were purified prior to use by





passing carbon dioxide through the molten salt for 24 hours, to remove traces of oxide and hydroxide.

Ruthenium, rhodium, palladium, platinum, gold and silver were corrosion tested for 100

hours at 650°C with purified carbonate (62 : 38 mol per cent lithium carbonate : potassium carbonate) under a 68 hydrogen, 17 carbon dioxide and 15 per cent water vapour atmosphere. These conditions simulated those at the anode side of a molten carbonate fuel cell. The samples appeared unmarked at the end of the test period and had suffered no significant weight change. Such changes are recorded in Table I, together with those for 321- and 304-type stainless steels which were tested under identical conditions.

The results for platinum and silver appeared surprising in view of the fact that corrosion under carbon dioxide has been reported previously (6). In the current work, however, hydrogen was also included in the gas atmosphere; and no trace of the previously reported lithium platinate was found by X-ray photoelectron spectroscopy (XPS).

The 100 hour corrosion test was repeated for platinum and silver in an oxidising atmosphere of 50 per cent carbon dioxide, 50 per cent air. Under these conditions silver had visibly dissolved in the carbonate and some had plated out onto the bottom of the crucible. The corrosion of silver under oxidising conditions is consistent with data in the literature (7). The

Table I
Corrosion Test Results
(Li₂CO₃ : K₂CO₃ 62 : 38 mol%: under 68% H₂, 17% CO₂, 15% H₂O at 650°C)

Material	Test duration, hours	Initial weight, grams	Weight change, per cent	Weight change, grams
Rhodium	93.6	0.604	0.33	-0.002
Ruthenium	93.6	0.940	0.21	+0.002
Platinum	93.1	0.369	0.54	+0.002
Palladium	93.1	0.816	0.49	+0.004
Gold	90.2	2.060	0.00	0.000
Silver	93.6	1.760	0.08	+0.001
321-type Stainless steel	90.1	0.419	2.10	+0.009
304-type Stainless steel	90.1	0.921	1.80	+0.017

Table II Contact Angle Measurements (Li ₂ CO ₃ : K ₂ CO ₃ 62 : 38 mol%; under H ₂ at 650°C and CO ₂ at 600°C)		
Material	Gas atmosphere	
	H ₂	CO ₂
Platinum	22	42
Palladium	40–42	38
Rhodium	68–70	38–40
Ruthenium	89–90	Wets
Silver	46	42
Gold	66	Wets
321-type Stainless steel	20	Wets
304-type Stainless steel	Wets	Wets

platinum sample had changed colour, and when studied by XPS the surface layer was found to be Li₂PtO₃. These two metals are therefore considered to be unsuitable for use at the cathode side of the fuel cell.

Contact Angles

The contact angles of the platinum group metals with molten carbonate were measured using a hot stage microscope in order to assess their wettability, wetting being defined as a contact angle of 20° or less. The unit was mounted in a wall of a glove box and this enabled the test samples and the carbonate to be handled under carbon dioxide throughout the test procedure. Contact angles were measured on 1 × 1 cm foil squares, which were placed on the workstage together with a purified crystal of carbonate. The work chamber was evacuated to 10⁻³ mbar and then either hydrogen or carbon dioxide gas was admitted to a pressure of 300 mbar. The sample was heated and the contact angle was measured. The results are given in Table II.

Rhodium, ruthenium and gold exhibited a high resistance to wetting under hydrogen and

all of the samples showed improved wetting resistance when compared to 321- and 304-type standard austenitic stainless steels.

Conclusions

In current molten carbonate fuel cells nickel-chromium is generally used for the anodes. However, the platinum group metals do offer good corrosion resistance and non-wetting properties under reducing conditions, and may therefore find application. In addition, noble metals alloyed with standard materials may enhance the properties of anode components.

Acknowledgement

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Flammable Gas Detection

In the above named paper, which appeared in *Platinum Metals Rev.*, 1988, 32, (2), 50–60, a correction should be made on page 58, right hand column, line 3. Here the word "increase" should be "decrease"; the corrected sentence then being: "The adsorbed atoms form dipoles at the metal-insulator interface resulting in a decrease in the work function of the metal at the interface."