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The Au cathode in the system Li_2CO_3–CO_2–CO at 800 to 900 °C

Norman H. Hagedorn
National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135 (U.S.A.)

Abstract

The lithium–CO_2 battery has recently been proposed as an advanced concept for missions to Mars or Venus, planets with carbon dioxide atmospheres. This article discusses the initial evaluation of gold as a catalyst for the cathodic reduction of carbon dioxide in molten lithium carbonate. An attempt is then made to rationalize the experimental results by proposing a phenomenological model for the sequence of reactions at and around the electrode. Finally, inferences are made as to the viability of gold as a cathode catalyst for the proposed battery.

Introduction

The possibility of missions such as a manned outpost on Mars, or a probe to the surface of Venus, has motivated researchers to consider developing electrochemical devices which might utilize the carbon dioxide atmosphere common to both planets. One such device is an alkali metal–carbon dioxide battery in which the carbon dioxide serves as the cathodic reactant. As presently envisioned, the device would utilize lithium as the anodic reactant, and the cell reaction product would be lithium carbonate, from which the lithium anode would be shielded by an as-yet hypothetical lithium-ion-conducting solid. The battery could be treated as a primary device, serving only until its supply of stored lithium was exhausted; as a secondary device, recharged chemically by resupply with lithium transported from Earth (which would, because of the low mass of lithium, be quite efficient); or, for the Mars mission, as a secondary device recharged electrochemically from an available nuclear central station power supply to regenerate the lithium. The last possibility is quite unlikely, since it would require a very high potential, evolving not only carbon dioxide at the anode, but oxygen as well. However, if energy were abundant and a premium were placed on the availability of an oxygen-containing process stream, perhaps an argument could be made for this option.

The following presents current results of experimental work to evaluate gold as a possible catalyst for the cathodic reduction of carbon dioxide. An attempt is then made to rationalize the experimental results by proposing a phenomenological model for the sequence of reactions at and around the

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electrode. Finally, inferences are made as to the viability of gold as a cathode catalyst for the proposed battery.

Experimental

Apparatus

The test cell used in this experiment is shown in Fig. 1. The 5-cm-diameter gold-plated nickel cup which served as the counter electrode was supported by a nickel disk suspended by nickel tie rods from a water-cooled cell cover. The cup was insulated electrically from the support disk by an intervening alumina disk. Alumina baffles were spaced above the cup to minimize thermal gradients due to radiation and convection. The water-cooled cell cover made possible the use of O-ring compression fittings enabling the vertical positioning of cell components such as the working and reference electrodes, reactant gas feed tubes and the cell thermocouple. The cell was enclosed in an alumina sheath and suspended in an Inconel 600 container which was, in turn, positioned vertically in a tubular furnace. The portion of the Inconel container that extended above the furnace was also water-cooled, ensuring the integrity of the rubber O-ring flange seal between the

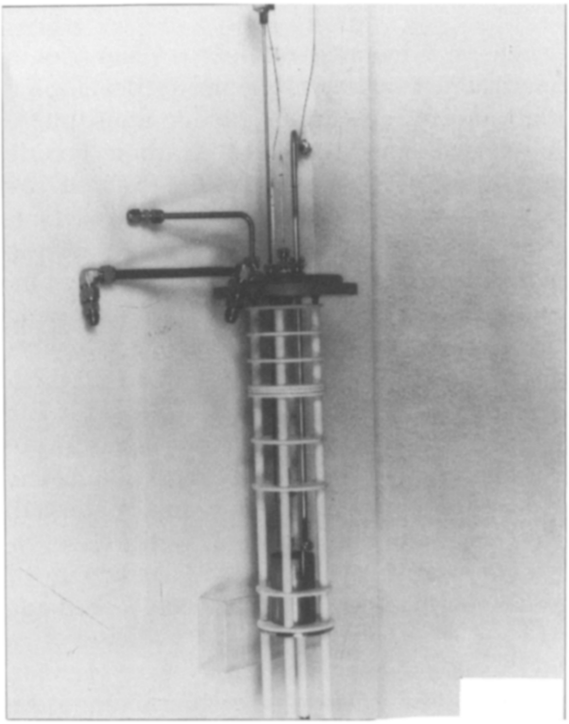

Fig. 1. Experimental cell showing water-cooled cover, tie rod suspension, thermal baffles, thermocouple, reactant feed and electrodes.

cell cover and the container, as well as that of those in the fittings in the cell cover. The use of O-ring seals made operation possible at pressures greater than one atmosphere.

The working electrode was 99.985 wt.% gold foil (Johnson Matthey, Inc.), 1 cm × 1 cm × 0.5 mm. After several configurations were tried, the reference electrode was modeled after Borucka [1]. When this electrode was lowered to the bottom of the cell, it trapped a portion of the carbonate melt and isolated it from the reaction products of the working and counter electrodes in the bulk melt. The reference electrode consisted of an outer 6.35-mm-diameter tube and an inner 3.18-mm-diameter tube, both of 99.8 wt.% alumina (Coors); 0.813-mm-diameter, 99.9 wt.% gold wire (Johnson Matthey); and assorted plastic fittings for sealing the electrode and connecting it to the gas supply system. The reference gas entered the electrode via the annulus between the gold wire and the inner tube, and exited between the inner and outer tubes. The outer tube, as described above, rested flush on the bottom of the counter electrode cup, trapping melt yet providing a thin-film high-impedance path for continuity between the trapped melt and the bulk melt of the cell. The inner tube extended about halfway down from the cell cover, and the gold wire continued to about 1 mm from the bottom of the counter electrode cup. Gold wire leads to the external circuit from the working and counter electrodes were enclosed in 3.18-mm-diameter alumina tubes and were externally sealed at the tube ends with epoxy resin. Prior to cell assembly, all gold electrode surfaces were washed in acetone, isopropyl alcohol, and deionized water.

The chromel–alumel (type K, ± 6 °C accuracy) thermocouple was sheathed in a 3.18-mm-diameter Inconel 600 tube with the lower 7.5 cm gold-plated. During the experiment, the thermocouple was positioned above the melt except when the melt temperature was being measured. The reactant gas feed was a 3.18-mm-diameter, 99.8% alumina tube that could be positioned to bubble the gas through the melt. The melt depth was 2.5 cm, and the working electrode was vertically centered in the melt and horizontally centered in the counter electrode cup.

Two reactant gases were used in the experiment: 99.99 mol.% CO_2 and an equimolar mixture (± 1% mixing accuracy) of 99.99 mol.% CO_2 and 99.3 mol.% CO. In use, the gases were dried in a molecular sieve column (type 4A, Union Carbide) and purified over copper turnings in an in-line tube furnace. Flows were set by hand and monitored with rotameters (Cole-Parmer, ± 2% accuracy). The Li_2CO_3 electrolyte (Fischer Certified ACS grade) was used as purchased.

Power to the cell furnace was regulated by a zero-firing solid-state relay actuated by a digital, solid-state microprocessor (Therm-Pro, Inc.). Stability was ± 2 °C. A model 273 potentiostat (EG&G Princeton Applied Research Corp.) was used for the electrochemical experiments, and that company's Electrochemistry Demonstration Program, Vol. I, in conjunction with an Apple IIe personal computer, was used to control transient tests and for the associated acquisition and presentation of data.

Procedure

The reference electrode was designed to permit the use of a separate reference gas, isolated from the working electrode reactant. However, for the experiments being reported, the composition of the reference gas was identical to that of the reactant gas stream, and cell potentials are reported as polarizations away from the rest potential. In practice, the reference electrode quickly became blocked, probably because the carbonate melt crept up the annular flow passages to a location cool enough for it to solidify. It thus became standard procedure to occasionally raise the reference electrode above the melt so that the gas in the outer tube of the electrode could become representative of the reactant stream, and then to return it to its operating position. Stability of the reference under this stagnant flow condition presented no difficulty during the short duration of the linear potential sweeps used as the standard technique to monitor the working electrode. Such stability could not be assumed during the acquisition of steady-state polarization data, when one data point could require half an hour or more. It was fortuitous under these conditions that the counter electrode, having a much greater active area than the working electrode, polarized only a few millivolts anodically under load and quickly returned to its rest potential when current flow ceased. In effect, it became a 'reference for the reference' and made it possible to sort out the recorded data.

As mentioned above, linear sweep voltammetry was used to evaluate the performance of the working electrode in response to changes in pressure, temperature and reactant gas composition, and to the presence or absence of bubbling through the melt. Generally, cathodic sweeps were made at 20, 40 and 80 mV/s to a polarization of -100 mV from the rest potential. The test parameters were total pressures of 1.2×10^5 and 2.1×10^5 N/m^2; melt temperatures of 800, 850 and 900 °C; reactant feeds of CO_2 and an equimolar CO_2–CO mixture; and a bubble rate, when used, of about 30 ml/min. Because of the cell configuration and the high conductance of the molten Li_2CO_3, about 5 $(\Omega\ \text{cm})^{-1}$ at 850 °C [2], *IR* corrections have not been applied to the measured currents. Because of the non-uniform current distribution on a flag working electrode surrounded by its counter electrode, currents are presented simply in milliamperes and not as current densities.

When switching from one reactant gas to the other, a laboratory vacuum pump (Leybold, Inc., model D1.6B) was used to exhaust the existing gas from the cell, and the cell was then repressurized with the replacement gas. In order to avoid bulk dissociation of the carbonate melt according to

$$CO_3^{2-} \longrightarrow CO_2 + O^{2-} \tag{1}$$

it was necessary first to cool the melt below its solidification temperature of 723 °C. When switching from pure CO_2 to the mixture, it was sufficient to carry out only one or two vacuum/repressurization cycles. However, going in the other direction, in order to completely remove the CO component from the cell, four of the cycles were executed, theoretically reducing the gas phase CO concentration to the order of 10 N/m^2.

To avoid melt dissociation according to eqn. (1) while at operating temperatures, it is necessary to maintain the partial pressure of CO_2 in the gas above the melt at values greater than the equilibrium dissociation pressure at the existing temperature. Some dissociation pressure data for Li_2CO_3 are presented by Janz *et al.* [2], but their results contain some uncertainties and extend only to about 850 °C. No data have been discovered relating the dissociation rate of the molten carbonate to the deficit between the existing CO_2 partial pressure and the equilibrium dissociation pressure, but it has been reported that the corresponding recombination rate for the ternary eutectic carbonate melt is generally quite slow [3]. In the light of the uncertainities, it is possible that, when operating at 900 °C and 1.2×10^5 N/m^2 with an equimolar mixture of CO and CO_2, melt dissociation was occurring. However, there is no experimental evidence for this, and no straightforward way to estimate possible effects if melt dissociation were occurring.

Another chemical process that one must be cognizant of is the Boudouard reaction for the partitioning of CO [1]

$$2CO \rightleftharpoons C + CO_2 \tag{2}$$

The reaction is favored thermodynamically by high CO pressure and low temperature. It has been pointed out [1] that, regardless of the cover gas composition, an electrochemical reaction at the surface of an electrode, by consuming CO_2 and generating CO, could create local conditions for carbon deposition. To estimate the 'worst case' scenario for the present experiment, a calculation based on data from the Joint Army–Navy–Air Force (JANAF) tables [4] for an equimolar mixture of CO and CO_2 at 827 °C and 2.1×10^5 N/m^2 total pressure indicates that a cathodic polarization of -150 mV from the rest potential could result in carbon deposition. This assumes very fast kinetics and negligible resistive loss, so that total polarization is Nernstian. Later discussion will argue that the reaction at the electrode surface does not produce the situation proposed above.

The working electrode surface was examined before and after its 9-day exposure to the carbonate melt at temperatures of 800 °C or greater. Scanning electron microscopy, with both secondary and back-scattered electron imaging, along with energy dispersive X-ray spectroscopy, were used in the analyses.

Results and discussion

Experimental results

Figure 2 presents linear sweep voltammograms for the gold cathode in Li_2CO_3 at 800, 850 and 900 °C, under an equimolar atmosphere of CO and CO_2 at a total pressure of about 1.2×10^5 N/m^2 (1.2 atm.). These data represent a baseline for the effects of other parameters, including aging at cell temperature. Some of these effects were quite surprising, in light of the original assumption that the cathodic process would reduce dissolved CO_2

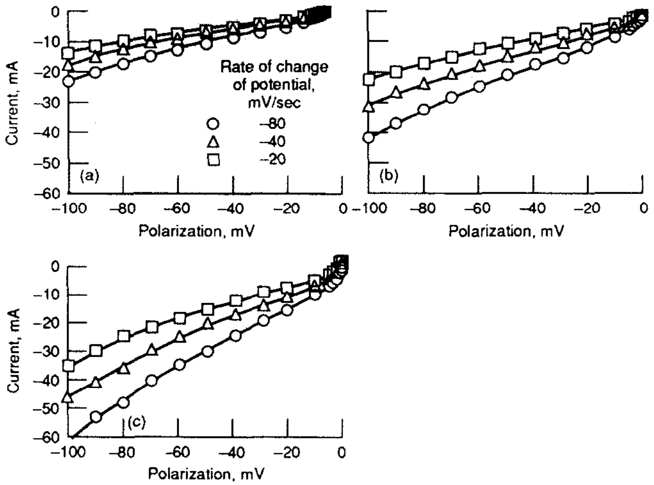

Fig. 2. Baseline linear sweep voltammograms. Gold electrode with Li_2CO_3 melt; gas feed, CO/CO_2; pressure, 1.2 atm.; with bubbling: (a) 800 °C; (b) 850 °C; (c) 900 °C.

diffusing from the melt. In the simplest case, the linear sweep voltammograms for such a process would have shown a current peak as the diffusional gradients developed, then a fall off to a steady limiting current until the potential became adequate to promote some new reaction [5]. However, the potential sweeps in Fig. 2 indicate no approach to a limiting current. Rather, the inflection of the curves toward the ends of the sweeps shows an increasing gradient of current with applied polarization. At much greater cathodic polarizations, one can expect the deposition of carbon, or even alkali metal, with very rapid reaction kinetics [6]. But, at the cathodic limit of -100 mV adhered to for the cathodic sweeps in this experiment, it is assumed that such depositions have not occurred, and that the overall thermodynamic process can be represented as

$$2CO_2 + 2e^- \longrightarrow CO + CO_3^{2-} \tag{3}$$

However, the actual sequence of physical, chemical and electrochemical steps comprising this process becomes a matter of conjecture.

The most arresting result of this work was that electrode performance was very poor in the presence of CO_2 alone, but quite good when the reactant gas was a mixture of CO_2 and CO. Figure 3 presents cathodic potential sweeps at -40 mV/s before and after changes in the reactant gas, and reveals several salient characteristics:

(i) a loss in performance (e.g. from -18 to -7.5 mA at a polarization of -100 mV) after switching from the CO_2–CO mixture to CO_2 alone;

(ii) a further loss in performance, from -7.5 to -2 mA, during six days of evaluation of the Au cathode in CO_2;

(iii) a recovery, from -2 to -4 mA, due to return to the CO–CO_2 mixture;

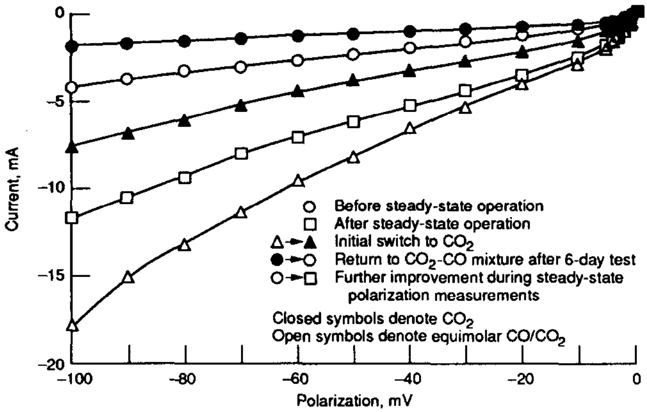

Fig. 3. Effect of reactant composition on performance. Gold electrode with Li_2CO_3 melt; potential sweep rate, −40 mV/s; temperature, 800 °C; pressure, 1.2 atm.

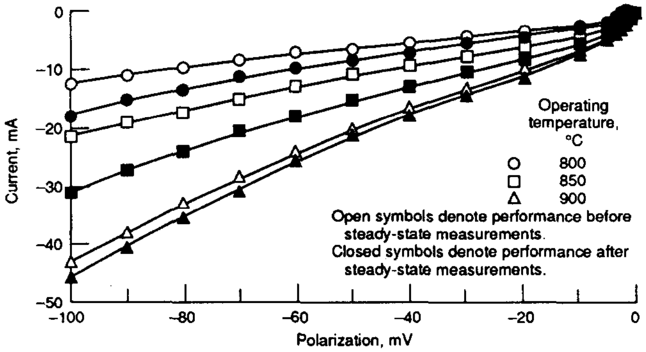

Fig. 4. Performance before (upper curve) and after (lower curve) acquisition of steady-state data at 800, 850 and 900 °C. Gold electrode with Li_2CO_3 melt; potential sweep rate, −40 mV/s; gas feed, CO–CO_2; pressure, 1.2 atm.

(iv) a subsequent additional recovery to −12 mA following several hours of quasi-steady-state operation under the CO–CO_2 mixture, during which steady-state polarization data were acquired.

This last characteristic, an improvement engendered by extended periods under load, was consistently observed when working with the CO–CO_2 gas mixture, as shown in Fig. 4. The two curves at each temperature indicate performance, at a sweep rate of −40 mV/s, before (upper curve) and after (lower curve) the collection of steady-state polarization data. This improvement was not consistently in evidence when operating with CO_2 alone. Rather, in that case, the time spent under quasi-steady load conditions resulted almost equally in small gains or losses in sweep performance and seemed to be more affected by other aspects of electrode history, such as prior time at the existing temperature, time at open circuit or time raised from the melt.

The results of steady-state polarization measurements are shown in Fig. 5 for the CO–CO_2 mixture. Figure 5 shows excellent steady-state performance of the gold cathode when CO is present equally with the CO_2. In the same Figure, single data points at 800 and 900 °C indicate the effect when the reactant gas stops bubbling. Also, the data for 900 °C include measurements at 2.1×10^5 N/m^2, and unexpectedly show no pressure effect. Furthermore, it can be seen in Fig. 6 that increasing pressure actually inhibited sweep voltammograms, whereas one would anticipate, on the basis of eqn. (3), that increased total pressure would enhance performance.

Both systems were slow to equilibrate after load changes. With the CO–CO_2 gas mixture, tens of minutes could be required for the rate of change of potential under load to diminish to 1 mV/2 to 3 min, at which time data would be recorded; and up to 30 min was required to return to a stable open circuit value. With CO_2 alone, attainable currents were at least an order of magnitude less than with the gas mixture, and polarizations were greater. Response was so slow in both directions that a considerable degree of uncertainty exists for the recorded data. For this reason, Fig. 7 simply

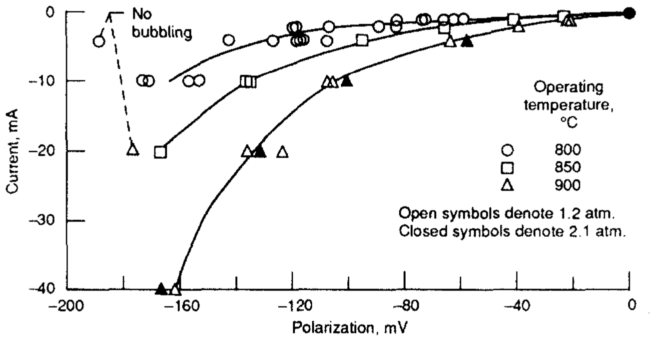

Fig. 5. Steady-state polarization data for equimolar CO–CO_2 mixture. Gold electrode with Li_2CO_3 melt.

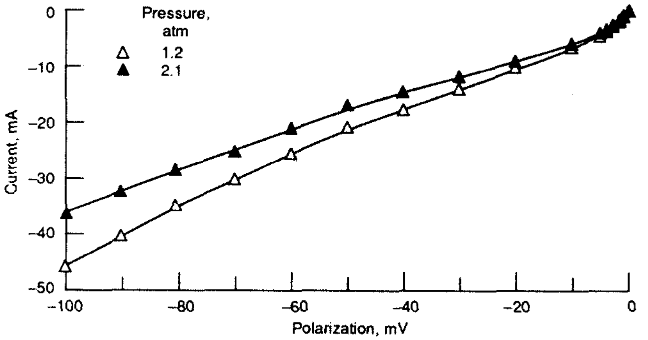

Fig. 6. Effect of total pressure on electrode performance. Gold electrode with Li_2CO_3 melt; potential sweep rate, −40 mV/s; temperature, 900 °C; gas feed, CO–CO_2.

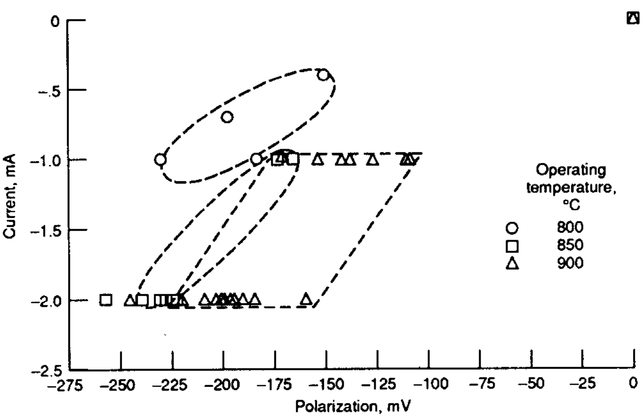

Fig. 7. Steady-state polarization data for CO_2 alone. Gold electrode with Li_2CO_3 melt; pressure, 1 to 2 atm.; with and without bubbling.

shows envelopes encompassing the data at a given temperature, without attempting to distinguish between the effects of total pressure or bubbling of the gas through the melt.

A phenomenological model

In order to rationalize the performance characteristics exhibited by the gold cathode in this experiment, it is hypothesized that the primary source of CO_2 being reduced at the cathode surface is not diffusion from the melt, but the dissociation reaction:

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-} \qquad (1)$$

At the electrode surface, reaction (1) would be promoted by the initial electrochemical consumption of any dissolved CO_2 at, or near, the electrode. (Note that reaction (1) would be retarded by an increase in total pressure or in CO_2 partial pressure, with the inhibiting effect noted in Fig. 6.)

It is also hypothesized that the buildup of the oxide ion at the electrode surface can strongly impede cathodic performance. Reaction (1) is an example of a Lux–Flood [7, 8] acid–base system in which the carbonate ion (the oxide ion donor) is the base, and carbon dioxide is its conjugate acid. Depending on the operating conditions and the processes occurring locally, the melt can become extremely basic near the electrode. This could significantly affect the overall reaction path by influencing the variety of electrochemically active species that could be present, including carboxy-ion intermediates such as CO^+ and CO_2^- [9].

The two systems (CO_2/Au and CO_2,CO/Au) in the molten ternary eutectic mixture of alkali carbonates were evaluated by Borucka [10] with regard to their suitability as reference electrodes in molten carbonates. Micropolarization was measured anodically and cathodically, with current densities in the order of 1 to 10 $\mu A/cm^2$. Exchange currents were estimated, and possible electrode processes were suggested. It was determined that the CO_2/Au electrode was extremely irreversible, with an overall process thermodynamically equivalent to a very dilute oxygen electrode,

$$1/2O_2 + CO_2 + 2e \longrightarrow CO_3^{2-} \tag{4}$$

governed by a very slow activation step possibly involving interaction between the gold surface and oxygen, a 200 ppm impurity in the CO_2. The exchange current for this electrode was shown to be about 1/30th that of CO_2,CO/Au.

Although the stability of gold oxides at the temperature and potentials under consideration is difficult to defend thermodynamically, the observed behavior of CO_2 on the gold cathode supports the hypothesis of a process that is at least generically similar to that described. Therefore, for the sake of the present argument, it is simply assumed that oxide ions are preferentially adsorbed on the gold surface, presenting a physical impediment for access of CO_3^{2-} to the electrode and for the charge transfer process.

The preference for this explanation is partly based on the extreme slowness of the return to open circuit potential, especially in the presence of CO_2 alone, after sustaining a quasi-steady-state cathodic load. The timeframe appears more typical of relaxations associated with chemisorption bonds than of the diffusional dispersal of concentrated species in solution, especially when the melt is agitated because the reactant gas is bubbling.

The remainder of the proposed reaction model draws heavily on the work of Borucka [3] and Borucka and Appleby [9], in which the CO_2,CO/Au/CO_3^{2-} system was examined in relation to the oxidation of CO, as in a molten carbonate fuel cell anode. In particular, the CO_2^{2-} ion, proposed in ref. 3 and strongly supported by experiment and thermodynamic and kinetic arguments [9], is invoked here. The CO_2^{2-} ion was shown to be formed by the rapid reaction of CO and the O^{2-} ion:

$$CO + O^{2-} \longrightarrow CO_2^{2-} \text{ (fast)} \tag{5}$$

The CO_2^{2-} was further shown to be quite soluble in the molten carbonate, with solubility comparable to that of CO_2, about 3 times greater than that of CO [6]. Thus, eqn. (5) presents the process by which CO is able to depolarize the cathode of O^{2-} ions, promoting the supply of CO_2 reactant via eqn. (1). CO_2^{2-} is also produced in the cathodic charge transfer sequence, which can be indicated by the overall process

$$CO_2 + 2e \longrightarrow CO_2^{2-} \tag{6}$$

the reverse of which represented the 'second wave' in the oxidation of CO [3].

Finally, the reaction sequence is completed a short distance from the electrode by

$$CO_2^{2-} + CO_2 \longrightarrow CO + CO_3^{2-} \tag{7}$$

producing the expected products of the overall reaction and regenerating the CO for a continuation of the depolarization process at the cathode.

Obviously, eqns. (1), (5) and (7), when simply added, cancel each other. However, they convey a picture of the CO molecule functioning over a short distance, transporting O^{2-} ions from the cathode surface into the bulk melt via the CO_2^{2-} ion, and there being regenerated for return to the cathode. Thus, in spite of its relatively low solubility in the melt, the flux of CO to the cathode can be sufficient to depolarize the cathode because of the short distance the CO must diffuse from the saturated bulk melt.

In summary, the proposed cathodic sequence for the CO_2,CO/Au/CO_3^{2-} system, with (s) denoting the cathode surface and (b) the bulk melt, is, near the electrode

$$CO_3^{2-}(b) \rightleftharpoons CO_2(s) + O^{2-}(s) \tag{8}$$

$$CO(b) + O^{2-}(s) \longrightarrow CO_2^{2-}(b) \tag{9}$$

$$CO_2(s) + 2e \longrightarrow CO_2^{2-}(b) \tag{10}$$

Summing

$$CO_3^{2-}(b) + CO(b) + 2e \longrightarrow 2CO_2^{2-}(b) \tag{11}$$

In the melt

$$2CO_2^{2-}(b) + 2CO_2(b) \longrightarrow 2CO(b) + 2CO_3^{2-}(b) \tag{12}$$

and overall

$$2CO_2(b) + 2e \longrightarrow CO(b) + CO_3^{2-}(b) \tag{13}$$

In the absence of CO to effectively depolarize the cathode, the cathode must be depolarized via the slow [3, 6, 9] acid–base equilibrium (eqn. (1)) by CO_2 diffusing from the melt. A possible sequence might be

$$CO_3^{2-}(b) \rightleftharpoons CO_2(s) + O^{2-}(s) \tag{8}$$

$$CO_2(b) + O^{2-}(s) \rightleftharpoons CO_3^{2-}(b) \text{ (slow)} \tag{14}$$

$$CO_2(s) + 2e \rightarrow CO_2^{2-}(b) \text{ (slow, in the presence of excess } O^{2-}(s)) \tag{15}$$

with eqns. (14) and/or (15) controlling.

Electrode morphology

Figure 8 is a secondary electron image of the gold cathode surface after about 240 h at temperatures between 800 and 900 °C, during most of which the electrode was immersed in the molten Li_2CO_3. The large grains visible in the micrograph were not present at the beginning of the test. Figure 9 is an optical image of a cross section of a similar electrode that had not been at temperature as long but had been used as both an anode and a cathode. The picture reveals that the large gold grains can extend the full thickness of the 0.5-mm electrode flag. (Borucka [10] notes that after 6000 h at 800 °C in a ternary alkali carbonate eutectic, a gold electrode remained 'perfectly bright', developed very large surface grains, and did not dissolve, according to a spectroscopic analysis of the melt to a detection limit of 0.05 ppm.)

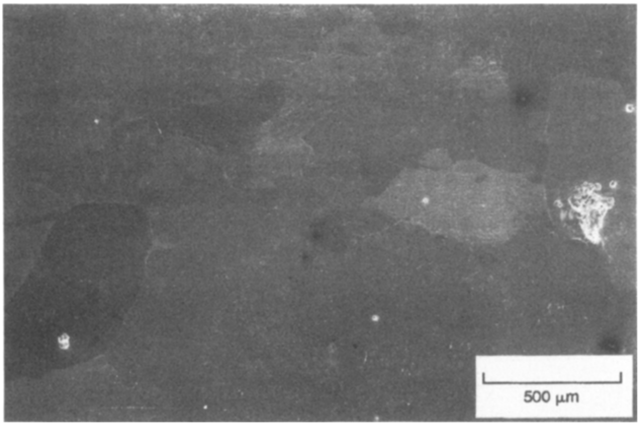

Fig. 8. Scanning electron microscope image of gold cathode surface after experiment showing development of large grains.

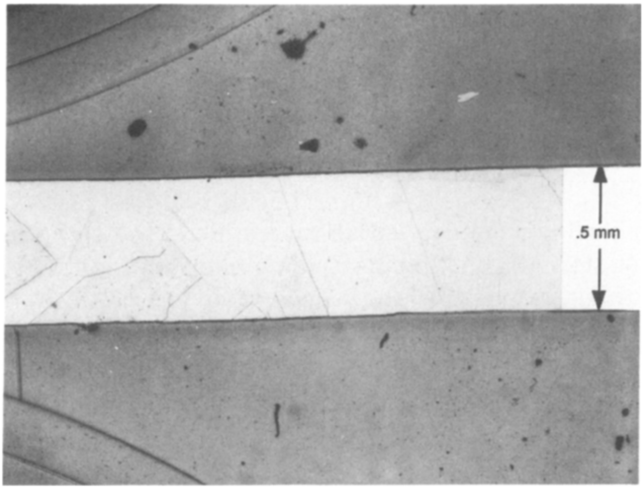

Fig. 9. Optical microscope image of cross section of gold electrode (lighter central segment) showing grain development to full depth.

The Au flag working electrode had fused to it a 6-cm-long, 0.813-mm-diameter Au wire at the other end of which, above the melt, was fused another Au flag for connection to the external circuit. The upper flag was never immersed and does not visibly appear to have undergone grain development, as did the working electrode. Thus, the grain development is not simply the result of exposure to high temperature, but is due to some combination of temperature, exposure to the molten carbonate, and electrochemical usage.

Another indication of the reordering of the gold electrode surface during testing is seen in Fig. 10, a scanning electron microscope image which shows a region with a large population of small crystals in the process of being

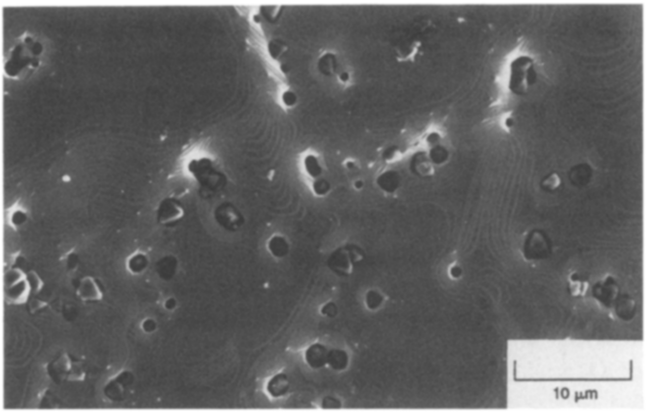

Fig. 10. Scanning electron microscope image of gold cathode surface after experiment showing encapsulation of ceramic crystals.

'swallowed up', as indicated by the contour lines encompassing each crystal. X-ray analysis of the crystals reveals aluminum and oxygen. Based on the bipyramid structure, it is assumed that the crystals are γ-$LiAlO_2$, since lithium is not detectable by the analysis and the γ-form is stable above 750 °C [6]. This material would be formed by surface disintegration of the alumina tubes of the reference electrode and the reactant gas bubbler, followed by the reaction

$$Al_2O_3 + Li_2CO_3 \longrightarrow 2LiAlO_2 + CO_2 \qquad (16)$$

Conclusions

With regard to the suitability of gold as a catalyst for the CO_2 cathode of a lithium–CO_2 battery, the results of the experiment reported here are generally encouraging. The most significant result is the evidence that CO must be present in the gaseous reactant feed stream of CO_2 to the battery cathode. In a functioning system this does not represent a problem, since CO is a product of the cathodic reaction and would be continuously rejected into the reactant gas stream. It would be a simple matter to recycle a portion of the effluent stream to build up the desired CO content. This is analogous to the recycling done in hydrogen–oxygen fuel cells to humidify a reactant inlet stream. The relationship between the amount of CO present and the activity of the gold electrode has not been established.

Of equal importance is the fact that, given the presence of CO in the reactant feed, gold allows the reduction of CO_2 to proceed at a high rate with moderate polarization. There was some loss of electrode activity during the 9-day experiment, but it is not clear whether this was due to an intrinsic characteristic of the electrode or was an artifact of the experiment. It was shown that the gold undergoes considerable morphological change at the test conditions and in a molten alkali carbonate environment. How this would manifest itself in a practical electrode design is open to conjecture. One can envision a finely divided gold catalyst dispersed on an appropriate current collector in such a way that the effect of the morphological changes would not be detrimental.

The conclusion from the experiment, that the primary cathodic reactant is, in a mechanistic sense, the carbonate melt, itself, has significance with regard to the design of a practical electrode. The electrode would not be subject to the traditional fuel cell electrode requirement of the 'three-phase interface', with its vulnerability to flooding and drying, for example, thus giving the electrode designer considerably more flexibility in approach. Nonetheless, access of the CO_2 and CO to and from the near-electrode region must be quite unrestricted. Considerable conceptual, experimental and modeling efforts will be required for development of a practical electrode.

The observed sluggishness in reaching steady-state operation after a change in load also requires mentioning. It may be that this is merely an artifact of the test cell geometry. If so, it must be resolved in the design of a practical electrode. If the problem is not so tractable, perhaps it can be resolved in a complete system by adequate power conditioning. This points out the need for some degree of system analysis early in the development of a defined mission.

Acknowledgements

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