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UCRL-TR-200209

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J.F. Cooper, R. Krueger

October 1, 2003

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This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

REACTIONS OF THE CARBON ANODE IN ALTERNATIVE BATTERY AND FUEL CELL CONFIGURATIONS

By

John F. Cooper¹ and Roger Krueger

Chemistry Directorate, Lawrence Livermore National Laboratory

¹Tel. 925-423-6649, Fax 925-422-0049, cooper3@LLNL

Abstract

A model is formulated by combining carbonate dissociation with pre-existing anode mechanisms involving heterogeneous reaction kinetics. The proposed model accounts for both the observed preponderance of CO₂ evolution and dependence of rate on carbon anode microstructure. Implications of the model for the design of carbon batteries and fuel cells are discussed, and the laboratory cells used in earlier research are described. High coulombic efficiencies for the net reaction $C + O_2 = CO_2$ require severely limiting the thickness of paste anodes in powder-fed fuel cells while the unreacting surfaces of solid prismatic anodes must be isolated from the CO₂ product atmosphere to prevent Boudouard corrosion, according to $C + CO_2 = 2CO$.

Background

Carbon/oxygen (air) batteries and fuel cells have been under development at LLNL in 1999-2001, under auspices of two internal research programs (Council on Energy and Environmental Systems¹, and Laboratory Directed Research and Development²). More recently, developments of advanced battery and fuel cell concepts have begun for application in arms-control verification and military electronics.³

The reaction of carbon and oxygen to form carbon dioxide may be sustained in galvanic cells operating in a molten alkali carbonate electrolyte at 600-800 °C. The reactions are normally written as:



The net reaction is the same as the combustion of carbon in air. Three aspects of these reactions are favorable to the prospects of practical carbon/air fuel cells and batteries. First, the net reaction [3] occurs without any substantial entropy change, so the Gibbs free energy ΔG is nearly equal to the standard enthalpy ΔH°_{298} (94.05 kcal/mol; 32.8 MJ/kg-C) at reaction temperatures of 600-800 °C. Second, the activities of elemental carbon and the product gas CO₂ are independent of extent of reaction and position in the cell, fixing anode potential and cell EMF. In principle, this allows a full utilization of the carbon in a cell at a fixed operating voltage. Finally, the reactivity of the carbon anode is highly sensitive to the micro- or nano-structure. Discharge rates at fixed anode overpotential (e.g., 0.2 V below $E^\circ = 1.02$ V, 750 °C) may vary by as much as four orders of magnitude between monoliths of graphite and of certain highly disordered carbons.

Reaction Products of the Carbon Anode

Experimentally, carbon anodes react in molten carbonate electrolytes with the evolution of both CO and CO₂. At substantial polarizations (> 0.1 V vs. theoretical), CO₂ is the predominant reaction product. Published studies have indicated this result through a variety of experimental techniques with various degrees of precision. Table 1 summarizes the historical background for carbon anodes in both carbonate electrolyte and in the cryolite based electrolytes of the Hall-Heroult aluminum smelting process.

Table 1. Methods used to confirm the four electron transfer for the anodic dissolution of carbon in mixed carbonate and cryolite/alumina melts, according to $C + 2O^{2-} = CO_2 + 4e^-$

Conditions	Method used	Ref.
T = 700 °C, graphite, carbonate	Weight loss; total gas evolution rate	Tamaru & Kamada ⁴
T = 400-900 °C, graphite, carbonate	Total gas evolution rate; gas analysis for CO, CO ₂	Hauser ⁵
T = 700-800 °C, coked lignite, carbonate	Gas evolution rates; some weight loss measurements	Weaver ⁶
T = 700 °C, particulate coal, coke, various graphitic carbons	Gas volumetric analysis, $d[CO_2]/dt = I/nF$	Vutetakis ^{7, 8}
T = 900-1100 °Cm cryolite/alumina, coke and graphite	$d[CO_2]/dt = I/nF$	Thonstad ⁹ Frank and Haupin ^{10, 11}

Physical Model Relating Structure to Reactivity and CO₂ Reaction Product

The anodic reaction of carbon has been widely studied for basic melts (carbonates) as well as acidic melts (cryolite). We suggest that the mechanisms might be similar. In both cases, the anodic reaction at high rates results in the predominate formation of CO₂. For temperatures above 650 °C, the Boudouard equilibrium ($C + CO_2 = 2CO$) would predict that CO would predominate. Haupin and Frank¹⁰ summarize early research in this area. Frank and Haupin et al.¹¹ of Alcoa report verbatim the mechanism [4-10], initiated by the dissociation of an alumino-fluoride species to form a free oxide ion [4]. This ion adsorbs on the surface and is discharged in two 1-electron steps to form a strongly bound -CO functional group at reactive carbon sites (such as edges or steps). This functional group will decompose to form free CO only very slowly.

A second adsorption of oxide onto the C_{RS}O site [8] is kinetically hindered, requires considerable over-potential and constitutes the rate-determining step for carbon oxidation to CO₂. Subsequent discharge of this adsorbed species occurs in two 1-electron transfers [9, 10] to form an unstable group -C_{RS}O₂ that is readily desorbed as CO₂.

Support for this model comes from the earlier experimental work of Thonstad^{9, 12} who measured Tafel slopes in cryolite melts and found them to be too great for the RDS to involve an electron transfer. He measured a subunity reaction order for oxide

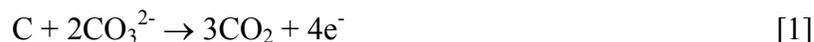
concentration. 0.56. This reaction order is consistent with reaction control involving a slow, heterogeneous absorption step as the rate determining step (RDS), as discussed by Vetter¹⁴.



Since the carbonate salts show a strong dissociation at 700 °C (yielding a mole fraction of oxide of 10^{-4} for the tri-eutectic^{17,18}), it is reasonable to replace [4] in Hall model with [4']



Reactions [4', 5-10] sum to the net reaction observed for carbon anode in molten carbonate melts [1; 11]:



C_{RS} is a carbon atom at a reactive site at an edge, defect, step or other surface imperfection in an otherwise stable graphene plane. Carbon materials high in defects and low in crystallinity are most reactive, as verified in our study².

Jomar Thonstad states that although the reaction order and Tafel slopes he reported in reference 9 indicate the mechanism [4-10], the origins are either Alcoa or Rolin¹²; Warren Haupin's associate Gary Tarcy at Alcoa reports the original idea might have come from either Piontelli or Calandra.¹³ No one seems to remember. I am referencing the Alcoa paper by Frank and Haupin¹¹ because it is the only one I have found that lists all the equations [4-10] verbatim while giving no other citation.

Implications in Cell Design for Batteries and Fuel Cells

Tilted and angled cell configurations.

The electrochemical cell used in this research consisted of a layered assembly of (1) a paste of particulate carbon in melt, (2) nickel mesh current collector, (3) melt-saturated zirconia fabric or felt, (4) porous nickel cathode and (5) a refractory metal cathode current collector.¹ This is the basic cell design of our pending patents.^{14, 15}

The efficiency of the cell requires careful control over the distribution of molten salt between the electrodes and separator. By placing this assembly at an angle to the horizontal, excess electrolyte drains from the anode and cathode surfaces, allowing access to the gas phase to the cathode and allowing egress of CO_2 from the carbon paste. The separator remains saturated with melt and impervious to gas flow. This

configuration prevents flooding of the cathode with melt and results in reproducible discharge curves of low polarization. This configuration was used in small-scale work (3 cm²) and in all scale-up tests (60 cm²), and provides a route to practical application on larger scales. Figure 1 depicts angled cells used in this research. On both small and larger scales, a stainless steel tube provided forced air convection.

On very small scales, simple capillarity may provide rapid drainage of excess electrolyte. In subsequent work with 50 cm² galvanic battery cells, we found it necessary to tilt the cell assemblies from horizontal to provide access of the air electrodes to air to promote formation lithiated-NiO and prevent the corrosion of the nickel and clogging with nickel carbonates

Problems in horizontal electrode configurations.

Early in the research, we found that cells using a nominally horizontal assembly of electrodes failed to give consistent or reproducible results. The problem was traced to the accumulation of molten salt on the air electrode in cases where the cathode surface comprised the lowest part of the cell. Under these conditions, the cathode became flooded with electrolyte. Such flooding is a universal problem with gas diffusion electrodes, which must bring three phases of matter (air, electrolyte, and current collector) into close proximity to provide the necessary reaction. More precisely, the air electrode structure must provide a thin layer of electrolyte (micron dimensions) across which oxygen and carbon dioxide may diffuse at a rate required for practical current densities.

One can calculate the maximum current density obtainable under conditions where the electrolyte fills the air channels of a gas diffusion electrode from Fick's diffusion law, with adjustment of the bulk diffusion coefficient for carbonate at 750 °C (~ 10⁻⁵ cm²/s; reference⁸) to compensate for the porosity of the air electrode:

$$D_{\text{eff}} = f^m D$$

Here f is the pore fraction (0.5) and m is a constant falling in the range of 2-3. The reaction cannot proceed faster than the flux of oxygen from the bulk to the reacting surface concentrated near the cathode/seperator interface:

$$\text{Flux} = i/nF = D_{\text{eff}} \Delta c/\delta$$

Where c is the concentration of oxygen in the melt (0.2 x 10⁻⁶ moles/cm³ at 750 C reference⁸) and δ is the thickness of the electrode (0.1 cm). Evaluating the maximum diffusion limited current density (i) gives a value on the order of 1-3 x 10⁻⁶ A/cm². In systems tested using the angled cell, current densities as high as 150 mA/cm² were obtained. The ability of cells with substantially horizontal orientation to produce any current at all (however irreproducible) is likely a consequence uncontrollable deviation from a horizontal or planar surface allowing some of the electrolyte to wick from the cell into the surrounding containment. Also, with small enough dimensions, the excess electrolyte might wick away from the electrodes by capillary action.

Our experience in cell design, fabrication and operation² resulted in several configurations that gave reproducible results. The angled cells of Figure 1A, B were the only configuration that has been used in scale-up in the original work² and formed the basis of a patent¹⁶ as well as ongoing research in large (50 cm²) primary battery cells.³

Early work with nominally horizontal cells was largely irreproducible until one of us (Krueger) suggested merely tilting the cells to provide a sufficient angle for rapid drainage (Figure 1 C). Close inspection of these nominally horizontal configurations (small scale, 2.8 cm²) indicated that orientation was generally not horizontal, but deviated by chance by varying amounts (Figure 2) because of assembly error or thermal distortion. Orientation is indicated in these photographs by the corrosion marks left on the alumina by each successive experiment with the same 2-cm ID tube.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Special thanks to the Council on Energy Environmental Systems and to Chemistry Technology Development for supporting this research. Special thanks are given to David Ahre (LLNL) for machining the 60-cm² cell.

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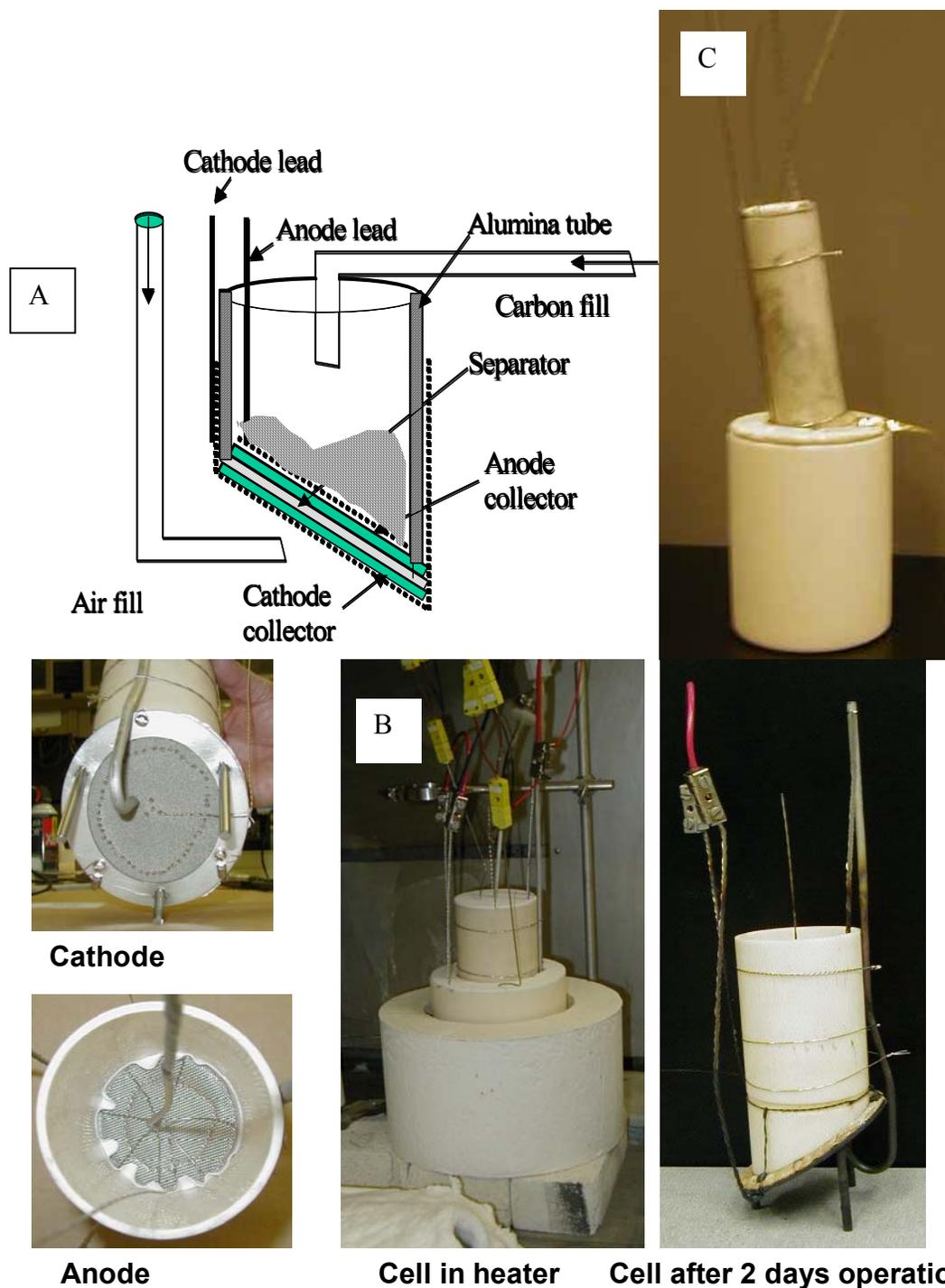


Fig. 1. A. The angled cell used in all scale up research on carbon/air cells is shown in the diagram. The electrode assembly is held at a 45-degree angle from horizontal. B. Four photographs of the 60-cm² cells are shown. This is the only configuration that was ever scaled to 60 cm². C. Significant bias in the orientation of the electrode assembly could also be achieved simply by tilting the cell with nominally horizontal electrodes, although such electrodes were never verifiably horizontal (see Figure 2, below).



Fig. 2. Three photographs are shown of nominally vertical cells of inside diameter, 2 cm (roughly 3 cm² working area), showing that the orientation of the electrode assembly (indicated by corrosion marks on the cells) were not controlled and generally were not strictly horizontal. Tilting the cell by an angle large compared with the angle of the electrode assembly (relative to horizontal) led to a substantial deviation from horizontal.