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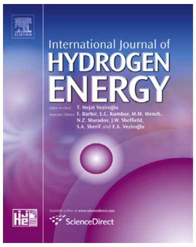

Analysis of the carbon anode in carbon conversion cells

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ABSTRACT

We examine further the electrochemical oxidation of carbon in molten carbonate, based on analysis of published research. Ascending and descending branches of voltage hysteresis found in current sweeps of atomically-ordered graphite and of disordered carbon (coal char) are separated by about 0.20–0.25 V and by 0.10–0.15 V for ordered and disordered forms, respectively, over a wide band of current density, 0.03–0.10 A/cm^2. The higher voltage of the descending branch is in rough agreement with prediction of the Y. Li model for the carbon/carbonate electrode in the same current range, for ordered graphite ($L_a = 70$–100 nm) and for disordered structures ($L_a = 3$–5 nm), respectively. We suggest that the amplitude of the hysteresis represents the difference between the overvoltage requirements for 2- and 4 electron net transfer processes, respectively. The 2 e− reaction ($C + CO_3^{2-} = CO + CO_2 + 2e^-$) dominates the low current segment (LCS) of our previous analysis, and the more hindered 4e− transfer reaction ($C + 2CO_3^{2-} = 3CO_2 + 4e^-$) dominates the high current segment (HCS). The voltage increase separating LCS from HCS is effected by accumulation of CO_2 within small, melt-filled pores to form highly supersaturated solutions of CO_2, which enhance anode voltage by a concentration overpotential of 0.10–0.25 V. Overpotential increases with reaction extent until (1) overall polarization inhibits the interior reaction and shifts CO_2 production to the more accessible exterior surface, or, (2) at a critical concentration (dependent on surface tension and pore diameter) bubbles nucleate and block current flow in the pores. Further support for this picture comes from the often-reported deviation of the gas composition from the CO/CO_2 ratio of the Boudouard equilibrium at atmospheric pressure, as open circuit conditions are approached in an electrochemical cell. Our interpretation accounts for the mole fraction of CO_2 at open circuit being greater than predicted from the Boudouard equilibrium.

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Introduction

A century-old goal of electrochemistry has been a fuel cell that could generate electricity from elemental carbon derived from fossil or biological resources. This would circumvent efficiency limitations of the Carnot cycle and avoid pollution associated with open combustion of coal or biomass. Electrochemical conversion of carbon to electric energy raises the possibility of reaching efficiencies of 80% of the maximum

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allowed by the Gibbs free energy for the reaction, $C + O_2 = CO_2$ [1,2]. There has been a resurgence of interest in research in this area within the last 5 years, with substantial efforts in China, Australia, Japan, Korea, Europe and the UK, as reviewed by Cao [3] and Giddey et al. [4].

Carbon anodes are studied in the electrolytes of the solid oxide fuel cell (SOFC) and the molten carbonate fuel cell (MCFC) in appropriately modified configurations. Recent advances have been reported by many in the area of mixed or hybrid electrolytes using both oxide and electrolytic conductors to facilitate the use of impure carbon fuels and exclude corrosion-prone metals from the cell. (see e.g., Zhu [25]).

This communication is a continuation of our analysis reported earlier [5]. For reasons cited there and elsewhere we have elected to focus our attention on cells using monolith or particulate carbon anodes in molten carbonate electrolyte, using $\{Li^+\}NiO$ cathodes, and operating at ca. 700 °C [6,7].

Background

Basic reactions and thermodynamic relations

Direct carbon conversion (DCC) cells using molten carbonate electrolyte may be described as a series of phases between two electronic current collectors. The cathode is Li^+ substituted NiO catalyst supported by a cathode current collector, CCC, of stainless steel. The anode is likewise porous, and both cathode and anode behave as porous or particulate electrodes. In the cathode the reactants are O_2 and CO_2 (introduced as gas but dissolved in the carbonate electrolyte), and the product is carbonate ion. In the anode the reaction mechanism and the transport phenomena are more complicated. The reactant is carbon dispersed as a slurry in molten carbonate or bulk carbon immersed in molten carbonate. In either case the carbon has micropores which may or may not be filled by carbonate melt. The reaction products of the anode are assumed to be mixtures of CO_2 and CO, which are either dissolved in the molten electrolyte or evolved as bubbles upon exceeding saturation to occupy an adjacent gas phase:

$$\mathrm{CCC//cathode//electrolyte\ matrix//anode//ACC} \tag{1}$$

$$\begin{gathered}\mathrm{e^-//\{Li^+\}NiO(s)/O_2, CO_2(g)/CO_3^{2-}(liq)//CO_3^{2-}(liq)/} \\ \times\mathrm{/CO_3^{2-}, CO_2, CO(liq)/C(s)//e^-}\end{gathered} \tag{2}$$

A number of reactions may be written for this cell description:

$$\mathrm{C + O_2 = CO_2} \quad \text{Net cell reaction,} \quad n = 4, \quad E^\circ = 1.023\mathrm{V} \tag{3}$$

$$\mathrm{O_2 + 2CO_2 + 4\,e^- = 2CO_3^{2-}} \quad \text{Cathode} \tag{4}$$

$$\mathrm{C + 2CO_3^{2-} = 3CO_2 + 4e^-} \quad \mathrm{4e^-}\text{transfer reaction,} \quad \mathrm{V^\circ eq, 5} \tag{5}$$

$$\mathrm{C + CO_3^{2-} = CO_2 + CO + 2e^-} \quad \mathrm{2e^-}\text{transfer reaction,} \quad \mathrm{V^\circ eq, 6} \tag{6}$$

$$\mathrm{CO_3^{2-} = CO_2 + O^{2-}} \quad \mathrm{K_{D,700\ C} = P_{CO_2} x_{O_2^-} \Big/ x^{2-}_{CO_3} = 6.99\ 10^{-8} bar} \tag{7}$$

It has been shown that linear algebra techniques may be used to infer possible reactions in systems at equilibrium [8,9]. For the carbon/carbonate half cell a minimum of three basis reactions, (e.g., equations (5)–(7)) suffice to fully describe the anode stoichiometry. Similarly, any linear combination of reactions (5)–(7) may be substituted for one of these reactions to yield an equivalent description of the anode. For example, subtracting twice reaction (6) from reaction (5) yields the familiar Boudouard reaction that occurs in the gas or liquid phases contacting the carbon, and depends on the total system pressure, P:

$$\mathrm{2CO = C + CO_2} \quad \mathrm{K_{B,T,P} = (CO_2) \Big/ (CO)^2} \tag{8}$$

At temperatures above 700 °C, the reverse of (8) may corrode carbon to form CO, which, being volatile and fugitive, may be lost from the cell leading to a decline in carbon conversion efficiency.

From a practical point of view there is high interest in a carbon fuel cell producing pure CO_2 product because of the very high efficiency that can be achieved in principle. Experimentally, it is convenient to express the relative strengths of reactions (5) and (6) in terms of an apparent valence–the number of Faradays of electronic charge delivered from the anode per mole of carbon oxidized. Theoretical efficiency is nearly unity because of the near-zero change in entropy:

$$\eta_{\mathrm{theor}} = \frac{\Delta G^o}{\Delta H^o} = \frac{\Delta H^o - T\Delta S^o}{\Delta H^o} \cong 1.003 \tag{9}$$

We showed earlier that the total electrochemical efficiency can be expressed as the product of (9) with factors incorporating Nernst losses (from reduced oxygen activity at cathode), voltage losses from electrode polarization and electrolyte ohmic dissipation, partial utilization of reactants, and coulombic efficiency referenced to a 4e- net transfer per mole of carbon. When these losses are taken into account for a rigid-carbon/air cell, the equation for total electrochemical efficiency can be accurately represented by a simplified equation:

$$\eta_{\mathrm{total}} \approx \eta_{\mathrm{coul}} \frac{\mathrm{V(i)}}{\mathrm{V^o}} \tag{10}$$

Here, the coulombic efficiency, η_{coul}, is defined as the apparent valence of carbon divided by 4.

Working model of the carbon anode

In earlier communications we examined published data on the carbon/carbonate anode in an effort to explain why some carbon materials and configurations are reported to have high electrochemical efficiency (70–80%) [10,11], while other studies report unacceptably high CO production leading to electrochemical efficiency below 50% [12,13]. We noted that most polarization curves show a distinct inflection that separates low- and high current segments (respectively, called LCS and HCS), that have different slopes and curvatures. Starting at open circuit, there is a rapid and nearly linear fall off of cell potential with current density (LCS). This is followed by a slower decrease in potential (HCS). When the experimental parameters associated with potential decrease were

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