

Kinetics of the Carbon Anode in Molten Salt

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One of the early goals of electrochemistry was development of a fuel cell that would convert elemental carbon into electric power and thereby avoid efficiency limitations of the Carnot Cycle and the pollutants from combustion. Interest in a direct carbon fuel cell (DCFC) was revived over the last decade as it became apparent that high efficiencies and useful power were achievable with systems based on equilibrium and non-equilibrium reactions involving disordered carbon materials produced from pyrolysis of fossil fuel or biomass [1]. Y. Li [2] proposed a reaction model based on the atomic structure of graphite. Cooper and Selman extended the model through analysis of published polarization curves and corresponding coulombic efficiency data, finding cases where efficiencies of 70-80% were indicated by cell voltage of 0.8 V and 99% coulombic efficiency [3, 4].

In a recent paper [5] we proposed an explanation for the wide divergence in reported total efficiencies for DCFC--from 50% to 80%--as resulting from different locations of the anodic reaction on (or within) the porous carbon electrode. Concentration of the reaction upon the exterior surface of the anode allows reaction overpotential to reach a critical level (0.15-0.25 V) which Li and co-workers found necessary to support an anode reaction resulting in a CO₂ product: $C + 2CO_3^{2-} = 3CO_2 + 4e^-$. Distribution of the reaction within the porous interior reduces current density to near-equilibrium levels of the electrochemical Boudouard reaction, $C + CO_3^{2-} = CO + CO_2 + 2e^-$. This cuts efficiency in half. Our interpretation predicts that efficiency may be maximized by selecting atomically disordered forms of carbon and filling the pores with inert material (e.g., pitch or off-eutectic salt). Alternatively, the reaction may be concentrated on the particle exterior by using anodes comprised of particles of high surface-area/volume ratio.

Here, we re-examine published off-gas data to explain how certain porous materials may develop sufficient overpotential to support a 4-electron transfer reaction sequence at high total energy efficiency.

Development of concentration overpotential in pores. Li et al. [2] developed a kinetic model of the anodic reaction of carbon in molten carbonate electrolyte that expressed rate as a function of the crystallographic parameter L_c – the characteristic dimension of stacks of graphene planes comprising the anode structure. The model finds CO₂ production requiring reaction overpotential of 0.15-0.25 V (depending on current density and temperature). The model does not explain why the reaction should shift abruptly from open circuit conditions (presumably resulting in off gas composition defined by the Boudouard reaction, $C + CO_2 = 2CO$) to a 4 e- pathway producing CO₂ at higher polarization. In fact, Table 1 shows measured off-gas composition does not necessarily approach Boudouard ratios at low or zero current density, as one expects for porous electrodes of high surface area [e.g., FC-12]. Dense anodes formed by heating and compressing coal show coulombic efficiency of 0.89 -0.97 at high current density (Table 1).

After prolonged exposure of the carbon electrode to the melt, it becomes fully wetted throughout the porous interior. When a fixed current is applied, a concentration overpotential ΔE_{conc} develops with accumulation of CO₂

dissolved in the melt within the pores, approximated by:

$$\Delta E_{conc} = (2.303RT/4F) \log (p_{CO_2})^3 \quad (1)$$

Concentration increases until the fugacity reaches the critical level at which a bubble may form and block the pore. We estimate this critical level by equating CO₂ pressure with the threshold for bubble nucleation, which depends on surface tension σ and critical diameter d_{pore} :

$$p_{CO_2, crit} = 4\sigma/d_{pore} \quad (2)$$

For $\sigma = 0.2$ N/m [6], the critical overpotential for CO₂ production according to the Li model (0.15-0.25 V) should occur at CO₂ fugacity in the range, 10-50 atm. This level may develop within pores of diameter < 800 nm (Table 2). Since the conductive carbon phase has a nearly uniform potential, the current flows to the exterior of the anode when bubbles impede current flow into the pores, supporting exterior carbon oxidation at a reaction overpotential equal to the concentration overpotential in the interior. We suggest that this critical combination of concentration overpotential and CO₂ fugacity accounts for the shift from low current segment to high current segment noted earlier for diverse carbon materials [5].

Table 1. Open circuit (Boudouard) efficiency compared with measured coulombic efficiency

Material	T, °C	η_{coul} Boudouard	i, mA/cm ²	η_{coul}^*
Pocahontas [5]	712	0.39	0	0.78
			10	0.73
			30	0.89
Peabody [5]	709	0.40	0	0.64
			20	0.66
			30	0.88
Kentucky No.9 [7]	710	0.40	100	0.97
FC-12 (porous, graphitized carbon)[5]	710	0.39	0	0.34
			12	0.40
			32	0.57
			52	0.68

* $\eta_{coul} = (1+r)/2(2-r)$, where $r = [CO_2]/([CO_2] + [CO])$ [3]

Table 2. Critical bubble pressure and pore diameter corresponding to assumed overpotential (Eqs. 1, 2).

ΔE , V	P_{CO_2} , atm	Pore diameter, nm
0.15	10	780
0.25	48	160

We conclude that concentration polarization developing within small dimension pores because of accumulation of mostly CO₂ product may elevate the anode potential by an amount promoting 4-e- transfer reactions producing pure CO₂ on the exterior surface. This maximizes energy efficiency. The inflection separating low- and high current segments in most polarization curves [5] may coincide with attainment of critical fugacity in the pores resulting in bubble formation, pore blockage, and abrupt shift in reaction site from interior surfaces to the exterior surface of the anode.

References

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