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Equilibrium thermodynamic aspects of the molten carbonate fuel cell ☆

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Abstract

A review of chemical equilibria in a molten carbonate fuel cell is given. In this device the composition of gases fed determines not only the voltage of the cell, but also the basicity of the molten electrolyte and, therefore, the chemical stability of electrode materials and of other solids used in the cell.

Keywords: Carbonate; Cell; Fuel; Stability; Thermodynamics

1. Introduction

A fuel cell is a galvanic cell which is continuously fed with fuel reagent at the anode and with oxidant reagent at the cathode. In the last few decades this old idea proposed originally by William Grove (1839) has been developed as a new concept of electric power production [1]. This concept consists of, (1) direct conversion of chemical energy of fossil fuels to electrical energy, (2) high efficiency (up to 60%) of this conversion, (3) modular construction of power generators permitting their dimensions to be fitted to the actual requirements, (4) absolute neutrality with respect to the natural environment (no emission of dust, negligible emission of SO_2 and NO_x). The only inconvenience of the application of fuel cells is the need to convert the direct electric current generated to alternating current.

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In the fuel cell natural gas (NG), coal gasification products (CGP), biogas (BG) and light petrol distillation products (PG) may be used as fuel to generate electric power. To date, however, the only electrochemical anodic reagent employed has been hydrogen. It exists as component in CGP, but must be produced by preconversion of the fuel-gas while using other fuel gases (NG, BG and PG).

2. Fuel cell efficiency parameters

For evaluating the fuel efficiency several parameters may be determined [1]. Let us mention the following definitions of these parameters.

(1) Thermal efficiency

$$\eta_{\mathrm{th}} = \frac{\Delta G_{\mathrm{f}}}{\Delta H_{\mathrm{f}}} = \frac{\Delta H_{\mathrm{f}} - T\Delta S_{\mathrm{f}}}{\Delta H_{\mathrm{f}}} \tag{1}$$

This is the maximum efficiency of a reversible isothermic cell. The free enthalpy of the reaction in the cell equals

$$\Delta G_{\mathrm{f}} = -nF\,\Delta E(X_{\mathrm{f}}) \tag{2}$$

where $\Delta E(X_{\mathrm{f}})$ is the electromotive force of this cell as function of the mole fraction X_{f} of the anodic process reagent available in the fuel-gas (available fuel). The enthalpy ΔH_{f} is the available fuel combustion enthalpy. It may be expressed as the sum of two parameters

$$\Delta H_{\mathrm{f}} = \Delta H_{\mathrm{wc}} + \mathrm{LHV}_{\mathrm{f}} \tag{3}$$

where ΔH_{wc} is the enthalpy of water condensation and $\mathrm{LHV}_{\mathrm{f}}$ is the lower heating value of the available fuel.

The fuel available in the fuel-gas may only be H_2 at room temperature ($X_2 = X_{H_2}$) but also CO and CH_4 at higher temperatures, when the conversion of these components to H_2 is also possible in the cell.

(2) Heating value efficiency

$$\eta_{\mathrm{h}} = \frac{\Delta H_{\mathrm{f}}}{\Delta H_{\mathrm{c}}} \tag{4}$$

where ΔH_{c} is the combustion enthalpy of all combustible species in the fuel-gas.

(3) Fuel cell system efficiency (without waste heat) determined as

$$\eta_{\mathrm{fs}} = \frac{\text{total electrical a.c. energy}}{\text{HHV raw fuel into fuel processor}} \tag{5}$$

The higher heating value (HHV) is the combustion heat of all combustible raw fuel-gas components. η_{fs} describes the efficiency not only of the cell but of all the systems comprising inlet-gas converters, the cell, outlet-gas and d.c. to a.c. current converters.

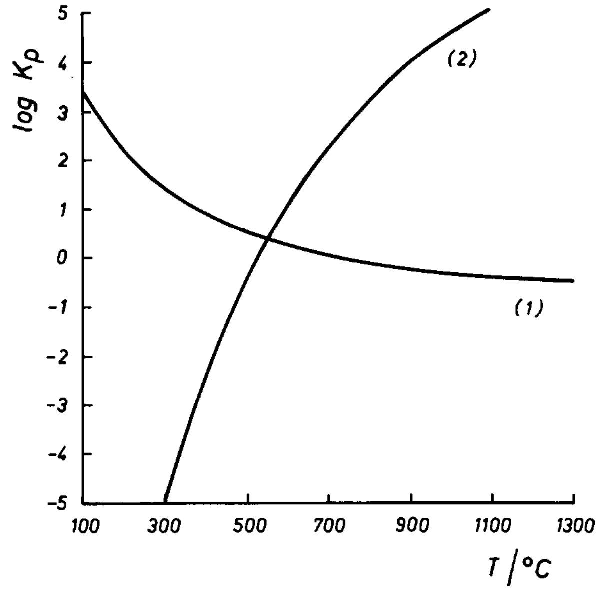

Fig. 1. The temperature dependences of the equilibrium constant values for reactions: (1) $CO + H_2O = CO_2 + H_2$ and (2) $CH_4 + H_2O = CO_2 + 4H_2$.

3. State-of-the-art and classification of fuel cells

In Fig. 1 are reported temperature dependences of equilibrium constant values for four reactions taking place in fuel-gas containing carbon, hydrogen and oxygen compounds (C–H–O fuel) [2]. The reported curves inform us within what temperature range the fuel-gases containing methane and carbon oxide may be converted to hydrogen. The higher the operating temperature of the fuel cell the better are the conditions for the preconversion of the raw methane containing fuel-gas using the waste heat of the cell process. This is an important criterion of reliability of the fuel cells now developed, which are classified according to the electrolytes used in them. This classification is reported in Table 1.

4. Advantages of molten carbonate fuel cells (MCFCs)

From data presented in Table 1 it is apparent that second generation fuel cells, (molten carbonate fuel cells (MCFCs)) are more promising than the first generation phosphoric acid fuel cells (PAFCs) [3]. The latter are now more developed and ready to commercialization; however, in the next decade, the former should reach the same level of technological realization. MCFCs will be then more attrative than PAFCs because,

Table 1
State-of-the-art of fuel cell development

	First generation	Second generation	Third generation
Operating temperature	60°C–205°C	≈650°C	≈1000°C
Symbol	AFC PAFC	MCFC	SOFC
Electrolyte	KOH H_3PO_4 Aqueous solutions	Alk. carbonate melts	Solid oxide electrolytes
Fuels for C compounds	C comp. CO ≤ 1.5% exclud.	C–H–O	C–H–O
Tolerance	CO_2 toler.	Good conditions for water–gas-shift reaction [a]	
Electrode	Pt catalyst	Ni based electrodes	
State-of-the-art	Space, traction ≤11 MW plants	250 kW stacks	Laboratory cells
Scale	Demonstration	R & D	Research
System	$\eta_{fs} \approx 40\%$	$\eta_{fs} = 50–60\%$	?, low polariz.

[a] Direct reforming of the fuel gas in the cell is feasible.

(a) they do not create catalytic problems, the kinetics of their electrode processes being fast;
(b) due to the water–gas-shift reaction (WGSR) the equilibrium of which is established in the anodic compartment of the cell, CO becomes an available fuel;
(c) high-grade waste heat is usable in reforming CH_4;
(d) their electrode and electrolyte materials, as well as other components, are not very expensive;
(e) the energy generation efficiency is the highest.

One must consider, however, numerous technical difficulties associated with the commercialization of MCFCs, such as corrosion of cell housing and separators, chemical instability of cathode materials, maintenance of long term stability of the operating parameters and many other problems which up to now have not been definitively resolved [4–6].

5. Chemical equilibria in the MCFCs

At the MCFC operating temperature (ca. 650°C) all chemical equilibria are easily and quickly established. The concentrations of all components of the complicated MCFCs chemical system are determined by the composition of fuel and oxidant

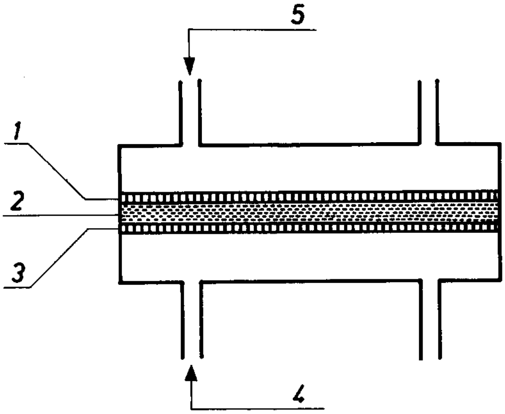

Fig. 2. The molten carbonate fuel cell as a chemical system composed of NiO (lithiated) porous cathode (1), molten alkali carbonate electrolyte in porous $LiAlO_2$ solid matrix (2), Ni porous anode (3), C–H–O fuel-gas (4) and $O_2 + CO_2$ oxidant (5).

gases. The system considered is open only for the exchange of materials through the gas phase and is closed with respect to the liquid phase of the electrolyte and solid phases of the electrolyte matrix, and to both anode and cathode materials. All parts of the MCFC as a chemical system are schematically reported in Fig. 2.

5.1. Basicity of the molten carbonate electrolyte

The chemical equilibria in the liquid and solid phases in the MCFC have been established as being dependent on the CO_2 and H_2O partial pressures in the gas phase. These parameters govern the basicity of the carbonate melts. The reactions determining the basicity and their consequences are reported in Fig. 3. When equilibrated versus gas phase composition the molten carbonate electrolyte is not only a binary (or ternary) alkali carbonate solution but is really an alkali carbonates + oxides + hydroxides reciprocal system. For calculating the concentrations of oxides and hydroxides the equilibrium constant values reported in Table 2 are to be used [7]. The values corresponding to those systems with binary or ternary eutectic solutions of molten carbonates show small deviations from ideality.

Using values reported in Table 2 one can establish the increase of the basicity for alkali molten carbonates in the sequence $K_2CO_3 \rightarrow (Na/K)_2CO_3 \rightarrow Na_2CO_3 \rightarrow \underline{(Li/K)_2CO_3} \rightarrow (Li/Na/K)_2CO_3 \rightarrow \underline{(Li/Na)_2CO_3} \rightarrow Li_2CO_3$. Two binary eutectic mixtures are underlined. The first of them, Li/K carbonate mixture, is commonly used as electrolyte in the state-of-the-art MCFCs. Recently, however, even more attention has been paid to the second, Li/Na carbonate mixture [3]. Physical properties and, therefore, the MCFCs, electrolyte parameters of these alternative melts are determined by the basicity dependence of the given property. Namely, with increasing basicity of the molten carbonate electrolyte, (a) the electrical conductivity increases, (b) the solubility of gases decreases, (c) the corrosion affinity to metals

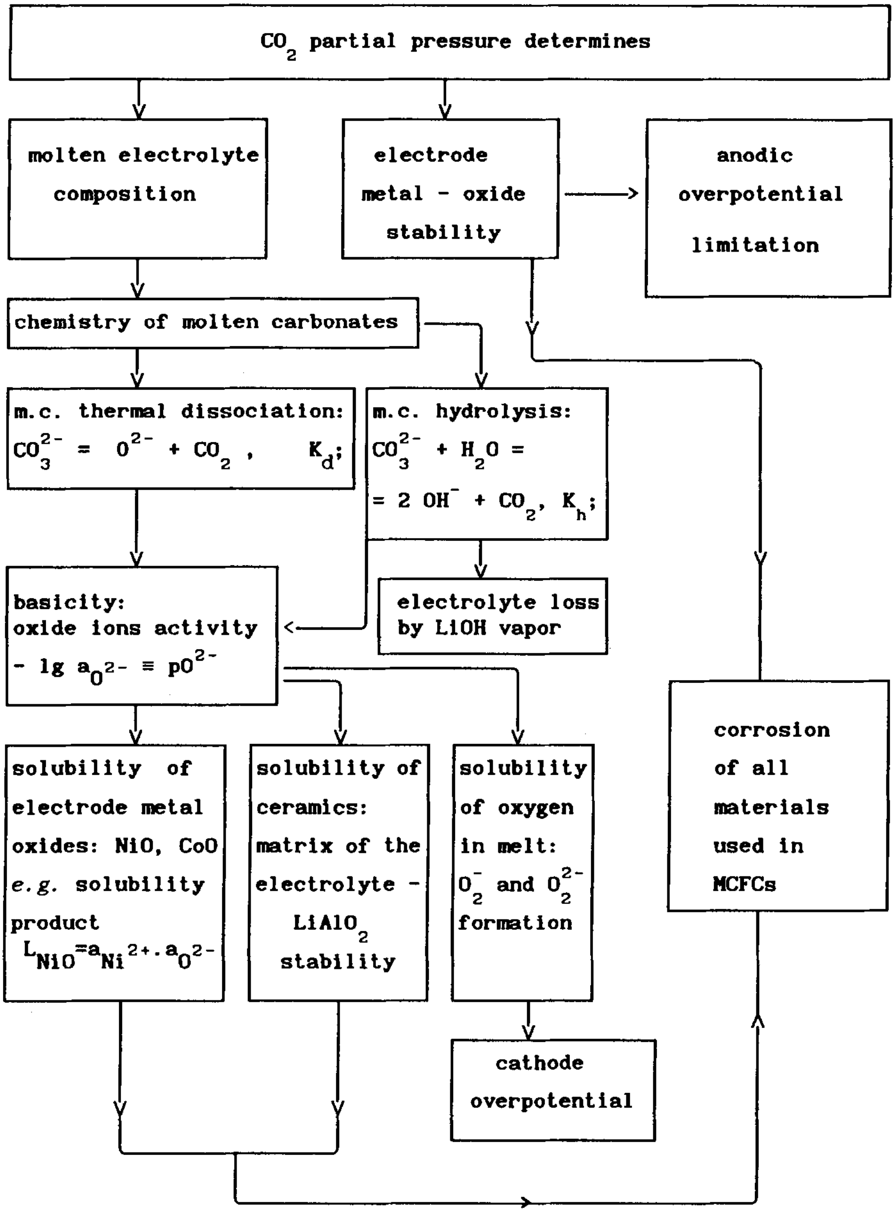

Fig. 3. Influence of fuel-gas composition on all chemical equilibria in the MCFC system. CO_2 partial pressure determines the basicity of the molten carbonate electrolyte and stability of solid phases.

decreases, (d) the stability of solid matrix material ($LiAlO_2$) decreases. The resulting choice of the most appropriate composition of the electrolyte consists in a compromise between the positive and negative aspects of the influence of melt basicity on the electrolyte parameters.

Table 2
Thermal dissociation and hydrolysis constants of molten alkali carbonates

	$\lg K_d \times T/1000$ [a]	$\lg K_h \times T/1000$ [a]
Li_2CO_3	$-9.97 + 0.006T$	$-4.56 + 0.002T$
Na_2CO_3	$-15.60 + 0.007T$	$-6.39 + 0.002T$
K_2CO_3	$-17.85 + 0.007T$	$-7.50 + 0.003T$
$53Li_2CO_3 + 47Na_2CO_3$	$-12.50 + 0.007T$	$-5.31 + 0.002T$
$50Li_2CO_3 + 50K_2CO_3$	$-13.81 + 0.007T$	$-5.83 + 0.003T$
$56Na_2CO_3 + 44K_2CO_3$	$-16.78 + 0.007T$	$-6.90 + 0.003T$
$43.5Li_2CO_3 + 31.5Na_2CO_3 + 25.0K_2CO_3$	$-13.53 + 0.007T$	$-5.70 + 002T$

[a] Temperatures are in kelvin.

5.2. Equilibrium electrochemical potentials of the MCFC electrodes

In the MCFCs electrode processes are as follows.

At the anode

$$H_2 + CO_3^{2-} \rightarrow CO_2 + H_2 + 2e^- \tag{6}$$

hydrogen as anodic reagent is produced also in reactions

$$CO + H_2O = CO_2 + H_2 \quad (6) \qquad CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{7}$$

(Water–gas-shift reaction) (Methane conversion)

The electrochemical potential of the MCFC hydrogen electrode is

$$E_{CO_3^{2-},H_2/CO_2,H_2O} = E^0_{CO_3^{2-},H_2/CO_2,H_2O} + \frac{RT}{2F} \ln \frac{P^a_{CO_2} P^a_{H_2O}}{a_{CO_3^{2-}} P^a_{H_2}} \tag{8}$$

where the activity of carbonate ion $a_{CO_3^{2-}}$ is 1, sum of the partial pressures of the anodic gases is $\Sigma P^a_i = P^a_{total}$

At the cathode

$$0.5O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \tag{9}$$

Arrows indicate the recrystalization of the anodic and cathodic process reagents.

The equilibrium electrochemical potential of the MCFC oxygen electrode is

$$E_{O_2,CO_2/CO_3^{2-}} = E^0_{O_2,CO_2/CO_3^{2-}} + \frac{RT}{2F} \ln \frac{P^c_{CO_2}(P^c_{O_2})^{0.5}}{a_{CO_3^{2-}}} \tag{10}$$

where $\Sigma P^c_i = P^c_{total}$.

5.3. The e.m.f. of MCFCs

The total MCFC reaction is

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{11}$$

Let us denote the equilibrium constants for this reaction as K_w.

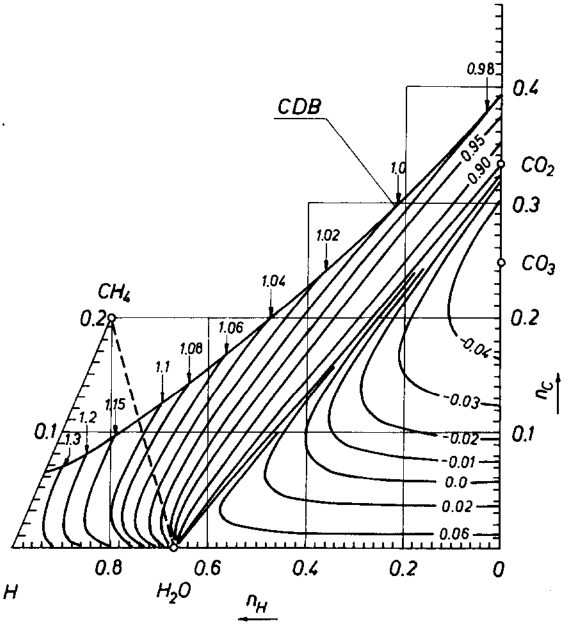

Fig. 4. Equilibrium composition of the C–H–O fuel-gas represented in H and C atomic fractions n_H and n_C, respectively: ($n_H + n_C + n_O = 1$), corresponding to the given e.m.f. values of the MCFC at 650°C and 1 bar. Dashed line, methane + water fuel mixture compositions; CDB, carbon deposition boundary.

When calculating the e.m.f. of the reversible MCFC both anode and cathode CO_2 partial pressures must be considered

$$\Delta E^{\mathrm{air,CO_2}}_{\mathrm{C\text{-}H\text{-}O}} = 4.31 \times 10^{-5} T \ln K_w + \frac{RT}{2F} \ln \left[\frac{P^{\mathrm{a}}_{\mathrm{H_2}} (P^{\mathrm{c}}_{\mathrm{O_2}})^{0.5}}{P^{\mathrm{a}}_{\mathrm{H_2O}}} \frac{P^{\mathrm{c}}_{\mathrm{CO_2}}}{P^{\mathrm{a}}_{\mathrm{CO_2}}} \right] \tag{12}$$

At 650°C the e.m.f. of the MCFC single cell fed by $0.8H_2 + 0.2CO_2$ gas mixture equals 1.04 V [1].

Let us emphasize that in these formulae P^{a}_i are coupled by chemical equilibria established in the C–H–O fuel. The calculation of the optimal e.m.f. depending upon gas-fuel composition is then an algebraic problem firstly solved by Cairns and co-workers [8–13]. One can see in Fig. 4 that for given C–H–O + H_2O fuel the highest values of the e.m.f. of the cell are obtained when solid carbon is deposited at the anode but in an infinitesimally small amount. In Fig. 4 a $CH_4 + H_2O$ mixture is represented by a dashed line. The diagram proves that the 1 : 2 stoichiometric conversion mixture is just appropriate to get the optimum e.m.f. of the cell at about 650°C.

From the functional relations among P^{a}_i ($P_{\mathrm{H_2}}$, $P^{\mathrm{a}}_{\mathrm{CO_2}}$ and $P_{\mathrm{H_2O}}$) it is apparent that the fuel-gas pressure dependence of the e.m.f. of the MCFCs does not follow the simple Nerstian coefficient. With the increasing fuel-gas pressure the e.m.f. also increases, but the equilibrium (7) is shifted to methane formation.

In the state-of-the-art MCFCs the fuel-gas is used under 3 bar pressure; there is now a tendency to increase this parameter to 10 bar.

Similarly the temperature dependence of the e.m.f. is not simply Nerstian, but within the 600–700°C temperature range the decrease of this parameter is about 84 mV K^{-1} [1].

5.4. Cell voltage and fuel-gas utilization

Under MCFC operating conditions, when the cell is generating current, one can calculate the actual fuel-gas composition as corresponding to the e.m.f. value equal to the actual cell voltage. This voltage depends on the available fuel (hydrogen) utilization parameter defined [1] as

$$U_f = \frac{n_{H_2(\text{inlet})} - n_{H_2(\text{outlet})}}{n_{H_2(\text{inlet})} + n_{CO(\text{outlet})}} = \frac{f_{\text{in}}[X_{H_2} + X_{CO}] - f_{\text{out}}[X_{H_2}]}{f_{\text{in}}[X_{H_2} + X_{CO}]} \tag{13}$$

where n_i are number of moles of the given gas components at the inlet and outlet of the cell, f_{in} and f_{out} are the total gas flow rate at the inlet and outlet of the cell, respectively.

The hydrogen utilization in the cell results in the anode electrochemical overpotential which, due to the speed with which equilibrium is established, may be considered equal to the difference between the reversible anode potentials corresponding to the initial and actual C–H–O fuel-gas composition. With the increasing fuel utilization parameter the fuel-gas composition changes along the fuel oxidation path (FOP) [12,13]. This line is reported in Fig. 5 for the C–H–O fuel-gas of standard composition $4H_2 + CO_2$. Along this line the operating cell voltage (considered quasi-reversible versus the actual fuel composition) may be calculated as depending on the fuel-gas utilization parameter. The FOP of the given fuel-gas composition is limited by its intersection point with the CO_2–H_2O line.

5.5. Stability of electrode materials

The anode overvoltage of the operating cell is limited by another equilibrium factor, the metallic nickel stability. This parameter as dependent on the electrode potential may be seen on the Pourbaix type diagram reported in Fig. 6 [14,15]. On this diagram the electrode potential defined according to formula (10) is presented as depending on the electrolyte basicity parameter pO^{2-} or on the $-\lg P_{CO_2}$ parameter (negative logarithm of CO_2 partial pressure). The diagonal scale presents the $-\lg P_{O_2}$ parameter values. On the diagram the metallic Ni and solid NiO stability limits are reported. The Ni/NiO coexistence line determines the oxidation potential of the Ni at the given CO_2 partial pressure (at the given basicity of electrolyte). Within the values of the last parameter corresponding to the MCFC

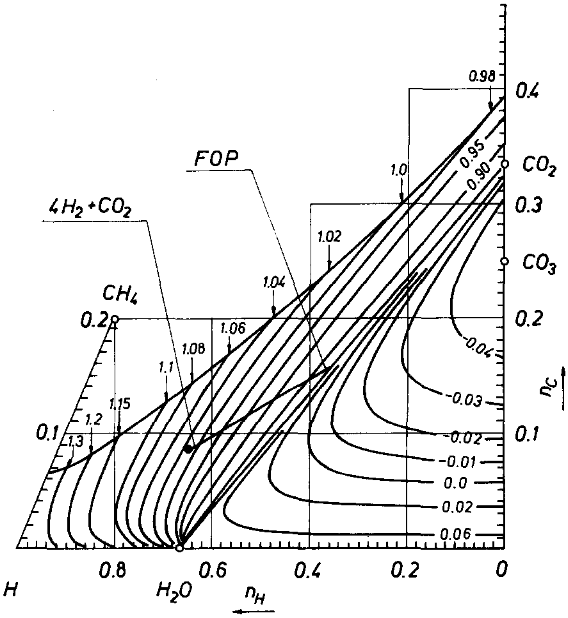

Fig. 5. Change of C–H–O fuel-gas composition, corresponding to the $4H_2 + CO_2$ mixture, during anodic oxidation of the fuel in the MCFC along the fuel oxidation path (FOP).

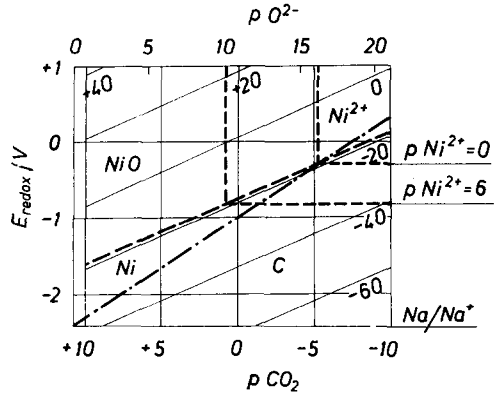

Fig. 6. Chemical stability boundaries, of electrode materials in the MCFC as functions of the electrolyte basicity and electrode electrochemical potential. – – –, Ni/NiO stability boundary: –·–·–, carbon deposition boundary. Stability regions of Ni^{2+} dissolved in molten carbonates within 10^{-6}–1 mol l^{-1} concentrations are also reported.

fuel-gas the nickel electrode is stable up to about −0.2 V of the anodic overpotential. At higher overpotential values nickel may be oxidized and the cell is fueled not only by the fuel-gas but also by the anode metal.

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