



Studies on sulfur poisoning and development of advanced anodic materials for waste-to-energy fuel cells applications

Fabio Zaza^{a,*}, Claudia Paoletti^a, Roberto LoPresti^a, Elisabetta Simonetti^a, Mauro Pasquali^b

^a ENEA R.C. Casaccia, Dep. Energy Technologies, Renewable Sources and Energy Saving, Via Anguillarese 301, 00123 Rome, Italy

^b University of Rome "La Sapienza", Dep. Chemistry, Materials and Environment Engineering, Via del Castro Laurenziano 7, 00161 Rome, Italy

ARTICLE INFO

Article history:

Received 8 September 2009

Received in revised form 13 January 2010

Accepted 17 January 2010

Available online 28 January 2010

Keywords:

MCFC

Hydrogen sulfide

Poisoning

Biogas

Bioenergy

ABSTRACT

Biomass is the renewable energy source with the most potential penetration in energy market for its positive environmental and socio-economic consequences: biomass live cycles for energy production is carbon neutral; energy crops promote alternative and productive utilizations of rural sites creating new economic opportunities; bioenergy productions promote local energy independence and global energy security defined as availability of energy resource supply.

Different technologies are currently available for energy production from biomass, but a key role is played by fuel cells which have both low environmental impacts and high efficiencies. High temperature fuel cells, such as molten carbonate fuel cells (MCFC), are particularly suitable for bioenergy production because it can be directly fed with biogas: in fact, among its principal constituents, methane can be transformed to hydrogen by internal reforming; carbon dioxide is a safe diluent; carbon monoxide is not a poison, but both a fuel, because it can be discharged at the anode, and a hydrogen supplier, because it can produce hydrogen via the water-gas shift reaction.

However, the utilization of biomass derived fuels in MCFC presents different problems not yet solved, such as the poisoning of the anode due to byproducts of biofuel chemical processing. The chemical compound with the major negative effects on cell performances is hydrogen sulfide. It reacts with nickel, the main anodic constituent, forming sulfides and blocking catalytic sites for electrode reactions.

The aim of this work is to study the hydrogen sulfide effects on MCFC performances for defining the poisoning mechanisms of conventional nickel-based anode, recommending selection criteria of sulfur-tolerant materials, and selecting advanced anodes for MCFC fed with biogas.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

From 1973 (oil crisis year) to 2005, in countries of Organization for Economic Co-operation and Development (OECD), the production of primary energy from renewable sources is raised from about 170 to 340 million tons of equivalent oil [1]. In particular, this trend is predominately due to the share of biomass, which, differing from other renewable sources, presents two different applications in energy sector:

- Direct production of energy, both electricity and heat, by means of biochemical and thermochemical process.
- Production of energy carriers with different chemical nature and physical state, such as biodiesel, bioethanol, and biogas.

Biomass penetration in energy market is driven by environmental and socio-economic politics. Related to environmental politics, biomass concurs to green house gas mitigation for preventing climate changes. As far as socio-economic politics concerned, bioenergy production promotes energy sources diversification for increasing global security for energy supply and reducing local dependence from fossil fuels exporter countries. Furthermore, in developing countries, sustainable productions of energy crops that do not compromise food productions, promote food security by increasing both food availability and food access. Increasing of food availability results from external benefits in food production, such as rural infrastructures improvement and agricultural productivities rise. This latter is due to biomass processing byproducts used as fertilizers. Increasing of food access is a consequence of new economic opportunities, promoted by alternative uses of rural sites [2].

Biomass is a no-fossil organic matter of either animal or vegetable origin, whose energy content came from solar energy conversion via photosynthesis. Due to its low energy content, it is necessary to extract chemical energy by high efficient technologies

* Corresponding author. Tel.: +39 06 3048 4004; fax: +39 06 3048 6357.

E-mail address: fabio.zaza@enea.it (F. Zaza).

such as fuel cells [3,4]. They are efficient energy conversion devices because do not present limits imposed by Carnot cycle. In addition they are environmental sustainable because do not contribute to noise and air pollutions.

The link between biomass and fuel cells is hydrogen. In fact, fuel cells are fed with hydrogen which can be produced by reforming of light hydrocarbons obtained by thermochemical or biochemical processing of biomass. It is important to note that bioenergy production via electrochemistry is convenient just coupling suitable types of biomass and fuel cells. In particular, biomass has to meet same requirements such as high content of the elemental hydrogen, available supplies, and low cost. These requirements are satisfied by animal, human and agro-industrial waste, which can be used to produce biogas, composed of methane and carbon dioxide mainly, by biochemical processing such as anaerobic digestion.

Biogas has many additional advantages, coming from both its chemical composition and the biomass from which it is derived. In fact the main component of biogas is methane, from which it is possible to obtain high yields of hydrogen because reforming kinetics for light hydrocarbons allow controlling byproducts formation. Also, due to the fact that biomass for biogas productions is animal, human and agro-industrial waste, bioenergy production has a double advantage of waste management and sustainable waste-to-energy production [5–7].

Fuel cells useful for bioenergy productions are those that work at high temperature because they are not poisoned by carbon monoxide, a typical fuels impurity, and because they are able to be directly fed with light hydrocarbons. Among high temperature fuel cells, molten carbonate fuel cells (MCFC) have an advanced technology that gives them an early potential market. In addition MCFCs have intrinsic advantages due to operating conditions and chemophysical characteristics of its components. MCFCs, in fact, work at 650 °C, optimal temperature for both the internal reforming and the utilization of the generated heat. In addition, they use a molten carbonate-based electrolyte, whose liquid physical state minimizes contact resistances with electrodes and allows the wet sealing.

Typical fuel for MCFCs is methane; therefore ideal system for bioenergy production from fuel cells is constituted by MCFC fed with biogas.

On the other hand, the utilization of biogas as MCFC fuel involves yet unsolved problems such as poisoning by impurities, in particular by sulfur. Hydrogen sulfide, which is the predominant sulfur compound in biogas, causes at low concentration the anode degradation and consequently the decay of cell performances such as power output and durability [8–13]. For overcoming the hydrogen sulfide poisoning issue, it is possible to act in different ways: controlling anaerobic digestion processes in order to mitigate hydrogen sulfide productions; optimizing desulfuration processes for reducing sulfur amounts to tolerable levels for the MCFC anode; developing advanced anode materials with high sulfur tolerance and effective recovery capability [14–16]. The aim of this work is to study hydrogen sulfide effects for defining sulfur poisoning mechanisms against nickel-based anodes, developing selection criteria of sulfur-tolerant materials and suggesting advanced anodes with high poisoning resistance and high recovering capability.

2. MCFC fed with biogas

Molten carbonate fuel cells are composed of a porous nickel-based anode, a porous nickel oxide-based cathode and molten carbonate salts as electrolyte within a porous lithium aluminate matrix. At the cathode side, oxygen and carbon dioxide react with each other to form carbonate ion. This latter migrates through the electrolyte until it reaches the anode. In this side, carbonate ion reacts either with hydrogen, forming water and carbon dioxide,

or with carbon monoxide which is eventually presents into the inlet anode gas, forming carbon dioxide. Half cell electrochemical reactions are as follows:

Cathode:



Anode:

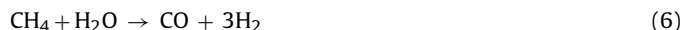


Corresponding overall cell reactions are as follows:



Molten carbonate fuel cells with internal reforming can be fed directly with light hydrocarbons rich gas such as biogas. Even if, biogas composition depends considerably on biomass compositions, process conditions (bacteria species, temperature, and pH) and the type of digester (covered lagoon, complete mix and plug-flow digester), it is possible to claim that the typical biogas composition is CH₄ (55–60%), CO₂ (30–45%), N₂ (1–5%), H₂ (1–5%), H₂S (80–4000 ppm).

Biogas is a suitable fuel for MCFC because methane is convertible in hydrogen by internal steam reforming reaction



This reaction occurs simultaneously with the electrochemical oxidation of hydrogen in the anode compartment, reaction (2). Carbon monoxide, derived from reaction (6), acts both as an hydrogen supplier via water–gas shift reaction



and as a fuel via anodic oxidation to carbon dioxide, reaction (3). Also, carbon dioxide takes part in dissociation reactions of carbonate ions, in such a way that it prevents the electrolyte loss by evaporation:



Finally, nitrogen is an inert component that acts as a safe diluent.

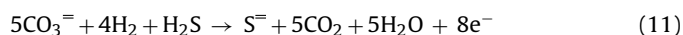
Unfortunately, biogas contains poisonous compounds such as halides, nitrogen compounds and sulfur compounds. Actually, hydrogen sulfide, which is the most predominant sulfur compound in reformed biogas, is the most harmful poison because it deeply affects cell performance even at low concentrations [17–20]. In particular, hydrogen sulfide interacts with all cell components via physical, chemical and electrochemical mechanisms.

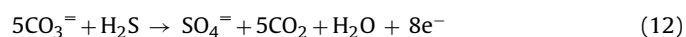
2.1. Electrolyte

Hydrogen sulfide reacts chemically with carbonates and forms either sulfide or sulfate ions reducing electrochemically active charge carriers. In this way cell performances decay, even if the ion conductivity of the electrolyte does not appreciably changes because carbonate ions are replaced by the same equivalent number of sulfur-based anions.

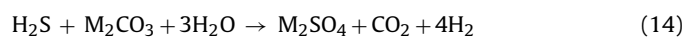
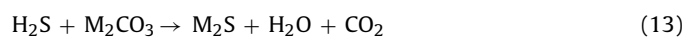


Hydrogen sulfide can react with carbonates also via electrochemical processes:





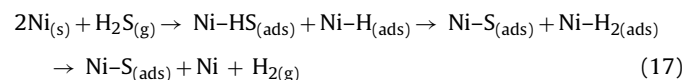
Standard potentials of above reactions are respectively -1.037 V and -0.986 V with respect to $\text{O}_2:\text{CO}_2 = 33:67\text{ vol}\%$ reference electrode. When the above anodic reactions occur instead of the hydrogen oxidation, the overall cell reactions are respectively as follows:



where M is a metal such as lithium or potassium.

2.2. Anode

Possible reactions of hydrogen sulfide with nickel can have different natures: formation of bulk nickel sulfides via chemical reactions, reaction (15); surface sulfuration either via physical adsorptions of hydrogen sulfide molecules, reaction (16), or via chemisorptions of sulfur atoms, reaction (17).



Furthermore in electrochemical cells hydrogen sulfide can react electrochemically with nickel-based anode and form nickel sulfides by oxidation of sulfide ions, dissolved in the electrolyte.



Chemical reactions generating nickel sulfides in bulk are thermodynamically forbidden at low hydrogen sulfide concentrations and at working condition of molten carbonate fuel cells. On the contrary, physical and chemical adsorptions of hydrogen sulfide on the nanostructured nickel-based anodes surface are thermodynamically allowed. Adsorptions are allowed at low hydrogen sulfide concentrations because of the large specific surface area of the nanostructured porous anode and quantum effects that become significant at the nanometer scale.

Electrochemical poisoning reactions occur when the anodic potential reach electrode potentials for nickel sulfides formation: the standard electrode potential for the half-reaction forming NiS and Ni_3S_2 are respectively -0.756 V and -0.829 V [17]. At open circuit voltage conditions, the anodic potential is more negative than electrode potentials necessary for either NiS or Ni_3S_2 formation. But at current load conditions, the anodic potential increases as a consequence of anodic overpotential effects and reaches necessary values for electrochemical nickel sulfides formation, causing the cell performances decay.

Poisoning mechanism depends on many factors such as applied current density, inlet anodic gas composition, operating temperature and pressure. Anyway, all sulfuration reactions affect chemophysical characteristics of the anode. In particular, they cause: block of both electrocatalytic sites for hydrogen oxidation and catalytic sites for the water-gas shift reaction; changes of the anode wettability toward carbonates; modifications of the anode surface and its porous structure; alterations of the anode conductivity.

2.3. Cathode

If carbon dioxide required for the cathode are satisfied by combusting and recycling the exhaust anodic gas, sulfur dioxides will

be in the cathode inlet gas. Anyway, there are limited literature data on the stability of nickel oxide-based materials in presence of sulfur dioxide.

3. Experimental

3.1. Experimental conditions

The molten carbonate fuel cell, used for studying hydrogen sulfur poisoning, was assembled with a porous lithiated nickel oxide-based cathode, a porous nickel-chromium alloy based anode and a tile made of a porous lithium aluminate matrix containing a carbonate salts binary solution with eutectic composition $\text{Li}_2\text{CO}_3:\text{K}_2\text{CO}_3 = 62:38\text{ mol}\%$. A 100 cm^2 class MCFC was used in this work in order to investigate the sulfur poisoning effects in bench-scale single cell testing. The effective geometric surface area of each electrode is 55 cm^2 , with an enhanced electroactive area due to their porosity. Experimental conditions were as follows: temperature 650°C ; pressure 1 atm ; composition of the cathode inlet gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37\text{ vol}\%$, composition of the anode inlet gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8\text{ vol}\%$, $40.5:54.7:4.8\text{ vol}\%$ and $33.3:61.9:4.8\text{ vol}\%$. It was used both dry and wet anodic gas. Flowing the anode inlet gas through a humidifier, which was heated at different temperature (65°C and 75°C), it was obtained wet anodic gas containing various amounts of water vapor. Different amount of hydrogen sulfide, such as 2 ppm , 26 ppm and 95 ppm , was introduced in anodic gas replacing part of the pure nitrogen flow with a flow of a certified gas mixture containing nitrogen and hydrogen sulfide with a suitable composition.

After 1100 h from start-up, the cell was fed alternatively with pure anodic gas and with gas containing different hydrogen sulfide amounts. Each anode gas fed the cell for about 30 h , necessary time for reaching steady state conditions, which was monitored by measuring cell voltage at different current density.

3.2. Characterization techniques

Cell performances were monitored by means of the Agilent N333 instrument. Investigations included measurements of cell voltages in galvanostatic conditions, from which polarization curves are obtained, and by the current interruption method, from which cell internal ohmic resistance is obtained. A custom-compiled LabView program was used to control the test rig and data acquisition.

Galvanostatic measurements were conducted by applying a constant direct current and recording cell voltages until it reaches a steady value. From these measures it was possible to construct polarization curves by graphing potential cells at steady state condition as function of applied currents.

The current interruption method was performed by applying a constant direct current and interrupting it quickly. The instantaneous cell voltage drop is related to internal cell resistance by Ohm's law. Cell voltage acquisitions are performed by a National Instruments acquisition card with an acquisition rate of 2000 sps .

The chemical characterization of the outlet anode gas composition was made by gaschromatography technique. The gaschromatography analyzer, Agilent 3000 Micro GC instrument, includes molecular sieve columns and thermal conductivity detectors. Argon was used as carrier gas to detect the amount of hydrogen residues in outlet anodic gas.

4. Result and discussion

Polarization curves of cells, fed with anode gas containing different hydrogen sulfide amounts, are shown in Fig. 1. The open circuit

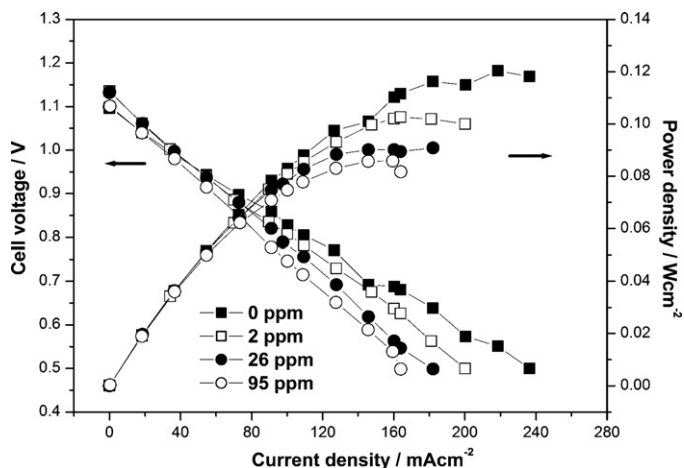


Fig. 1. Polarization curves for cells fed with anode gas containing different amount of H_2S : 0, 2, 26 and 95 ppm. Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%.

voltage (OCV) changes and depends on pollution levels because of secondary electrode reactions in competition with hydrogen oxidation. Electrode reactions generate a mixed cell voltage due to overall cell reactions (4), (5), (13) and (14) [18,21].

At low current density, hydrogen sulfide poisoning effects are negligible because the thermodynamically allowed reactions are not those of bulk nickel sulfides formation, but are just those of physical and chemical adsorption on anode surface and those of dissolution within the electrolyte. Vice versa, hydrogen sulfide effects are significant when current density is high, because electrode reactions produce nickel sulfides which block electrocatalytic sites on the anode surface.

The electrochemical mechanism of sulfur poisoning is more evident in Fig. 2, where cell voltage drops, due to poisoning effects, are graphed as function of current density. Cell voltage drops increase monotonally and linearly from 30 mA cm^{-2} when H_2S is 95 ppm and from 50 mA cm^{-2} when H_2S is 2 ppm and 26 ppm. Current density threshold, beyond which electrochemical poisoning occurs, depends on hydrogen sulfide amount because as high is hydrogen sulfide concentration as high is sulfide ions amount dissolved in the electrolyte solution. Consequently, electrode potentials for nickel

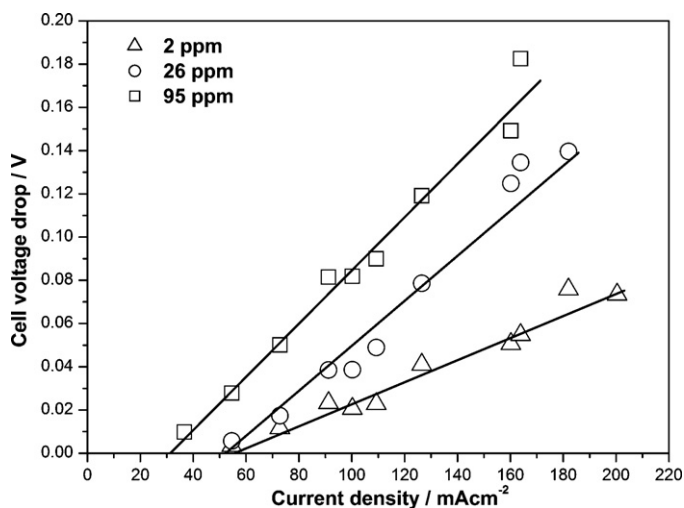


Fig. 2. Cell voltage drop as function of current density for cells fed with anode gas containing different amount of H_2S : 2, 26 and 95 ppm. Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%.

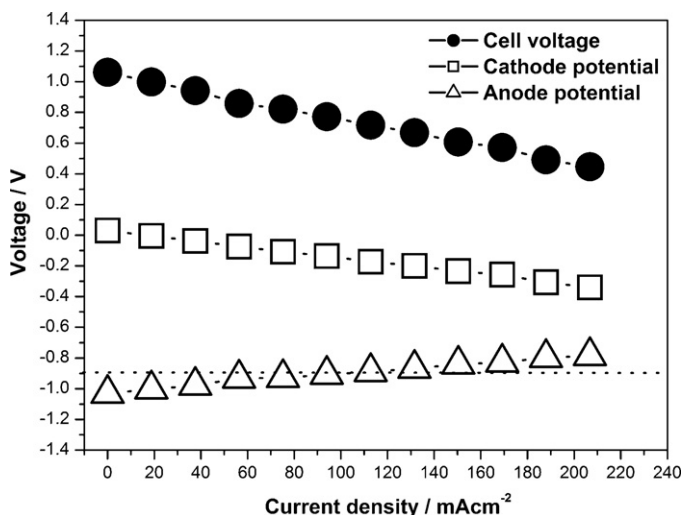


Fig. 3. Cell voltage and electrode potentials trends as function of current density for a cell fed with clean anode gas. Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%.

sulfides formation, reaction (18), decrease by Nernst equation:

$$E = E^0 - \frac{RT}{2xF} \ln[S^-]^y \quad (19)$$

Cell voltage drop increases with current density because sulfur poisoning occurs by means an electrochemical mechanism. In addition, because cell voltage drop and current density are linearly dependant with each other, Fig. 2, it is possible to claim an equation as follows:

$$\begin{aligned} \Delta V = A\theta &= A \frac{S_c}{S_T} = A \frac{S_c^{sp}}{S_T} n^{\text{H}_2\text{S}} = A \frac{S_c^{sp}}{S_T} \frac{y}{2x} n_{\theta}^{\text{H}_2\text{S}} = A \frac{S_c^{sp}}{S_T} \frac{y}{2x} \frac{I^{\text{H}_2\text{S}} t}{F} \\ &= \frac{AS_c^{sp} yt}{2xF} j^{\text{H}_2\text{S}} = \frac{AS_c^{sp} yt}{2xF} (j - j^{\text{H}_2}) \end{aligned} \quad (20)$$

where A and F are respectively a proportionality constant and the Faraday constant; ΔV is the cell voltage drop; θ is the fraction of covered surface; S_T , S_c and S_c^{sp} are respectively the total anode surface area, the covered anode surface area, and the anode surface area covered by one mole of H_2S ; $n^{\text{H}_2\text{S}}$ and $n_{\theta}^{\text{H}_2\text{S}}$ are respectively the total mole number of S^- electrochemically reacted and the total mole number of electrons produced by reaction (18); x and y are respectively stoichiometric coefficients of nickel and hydrogen sulfide in equation (15); t is poisoning time under a constant load current; $I^{\text{H}_2\text{S}}$ is the current generated by reaction (18); j , $j^{\text{H}_2\text{S}}$ and j^{H_2} are respectively the applied current density, the current density generated by reaction (18) and the current density generated by reaction (2).

In Fig. 3 are shown the anode and cathode potential as function of applied currents. At high current values, the anodic potential reach the calculated theoretical value for Ni_3S_2 deposition (-0.83 V vs. $E_{\text{CO}_2/\text{O}_2}$).

Furthermore, in Fig. 1 it is evident that cell performances decrease with increasing of hydrogen sulfide concentrations. Graphing cell voltage drops at 100 mA cm^{-2} as function of hydrogen sulfide concentrations, Fig. 4, it is evident that cell voltage drops increase progressively up to reach an asymptotic limit, related to anode surface saturation by formed nickel sulfides. This limit value correspond to the proportionality constant A in Eq. (20), because when the whole anode surface is covered by nickel sulfides, θ is equal to 1 and, consequently, ΔV is equal to the constant A .

Under such conditions that it is neglected the Nernst loss due to partial pressure gradients, cell performances can be expressed as

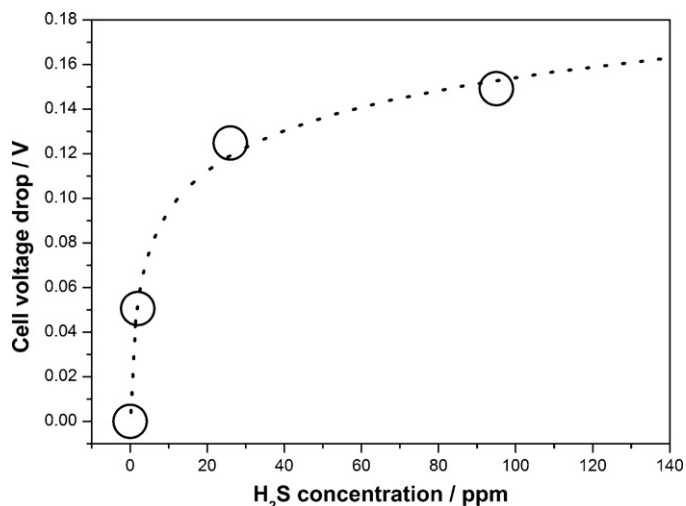


Fig. 4. Cell voltage drop as function of hydrogen sulfide concentrations for cells under an applied load of 160 mA cm⁻². Cell operating conditions: temperature 650 °C; pressure 1 atm; cathode gas O₂:N₂:CO₂ = 14.41:54.22:31.37 vol%; anode gas H₂:N₂:CO₂ = 47.6:47.6:4.8 vol%.

follows:

$$V = E - \eta_{\Omega} - \eta_p \tag{21}$$

where V is the actual cell voltage, E is the open circuit voltage, η_{Ω} is the ohmic loss and η_p is the polarization loss. From this equation, overvoltage values were calculated. Fig. 5 compares overvoltages obtained under current load at 160 mA cm⁻² for cells fed with different hydrogen sulfide amounts. It is evident that the ohmic loss is constant. It means that hydrogen sulfide does not affect the ionic conductivity of electrolyte, even if carbonate ions are partially replaced with sulfate and sulfide ions, and the electronic conductivity of the anode, even if sulfur-based ceramic compounds are formed on the metallic surface. In fact, graphing the internal resistance evolution time, Fig. 6, it is evident that internal resistance has the same value before and during poisoning.

Also, in Fig. 5 it is showed that the polarization loss rises with hydrogen sulfide concentrations because nickel sulfides formation affects both the activation polarization, blocking catalytic sites, and

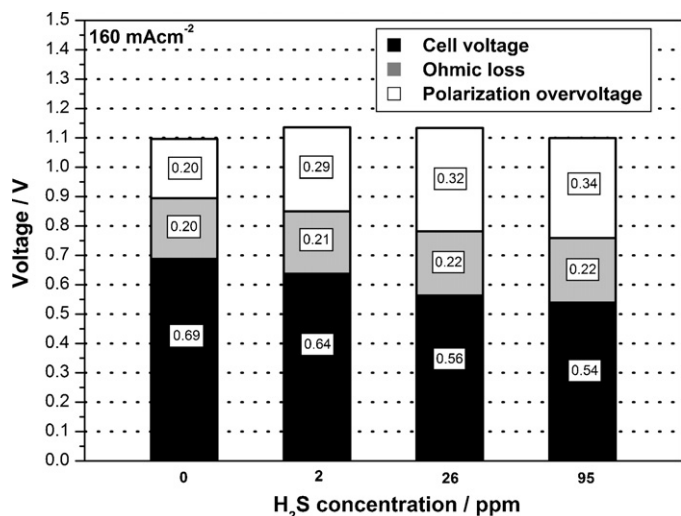


Fig. 5. Overvoltage contributions to cell performance loss under an applied load of 160 mA cm⁻² for cells fed with anode gas containing different amount of H₂S: 0, 2, 26 and 95 ppm. Cell operating conditions: temperature 650 °C; pressure 1 atm; cathode gas O₂:N₂:CO₂ = 14.41:54.22:31.37 vol%; anode gas H₂:N₂:CO₂ = 47.6:47.6:4.8 vol%.

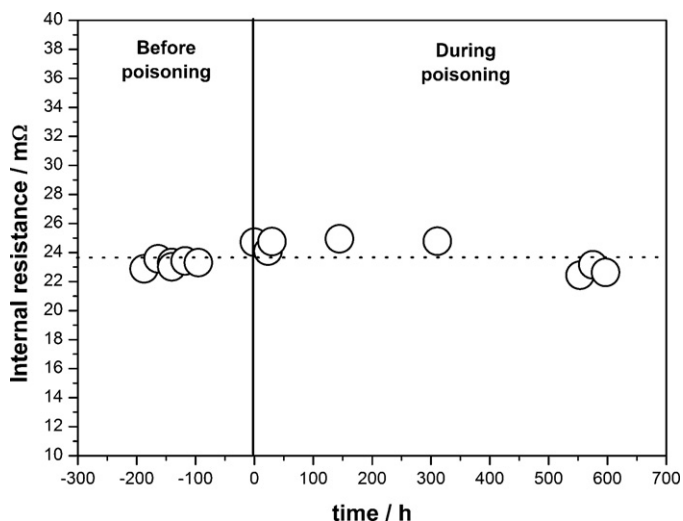


Fig. 6. Internal resistance evolution time before and during poisoning. Cell operating conditions: temperature 650 °C; pressure 1 atm; cathode gas O₂:N₂:CO₂ = 14.41:54.22:31.37 vol%; anode gas H₂:N₂:CO₂ = 47.6:47.6:4.8 vol% adding 2, 26 and 95 ppm of H₂S in sequence.

the concentration polarization, changing the structural properties of the anode and its wettability towards carbonates.

Fig. 7 shows chromatograms related to outlet anode gas of MCFC polarized at 160 mA cm⁻² and fed at the beginning with a clean gas and then with gas containing 2 ppm of H₂S. Residual hydrogen amounts in outlet anode gas are higher when MCFC is fed with dirty fuels. These experimental evidences are explained by the fact that electrons do not come from hydrogen oxidation alone, but from nickel sulfides formation too.

The effect of hydrogen on the poisoning capability of the hydrogen sulfide is shown in Fig. 8, where it is reported the cell voltage evolution time for cells fed with gas containing different hydrogen amount and 95 ppm of hydrogen sulfide. It is possible to see that as hydrogen amounts are lower as cell voltage drops are higher. This experimental evidence is related to two reasons. The first reason is that hydrogen sulfide adsorption depends on the hydrogen

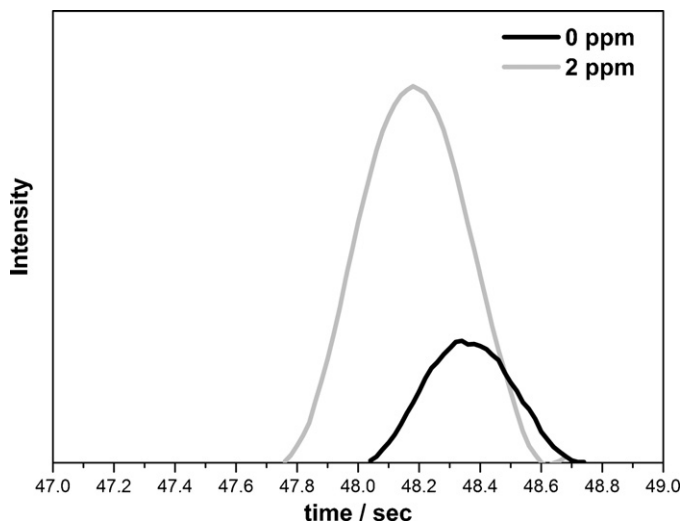


Fig. 7. Chromatograms of outlet anode gas from cells under an applied load of 100 mA cm⁻² and fed with anode gas containing respectively 0 and 2 ppm of H₂S: peak related to residual hydrogen. Cell operating conditions: temperature 650 °C; pressure 1 atm; cathode gas O₂:N₂:CO₂ = 14.41:54.22:31.37 vol%; anode gas H₂:N₂:CO₂ = 47.6:47.6:4.8 vol%.

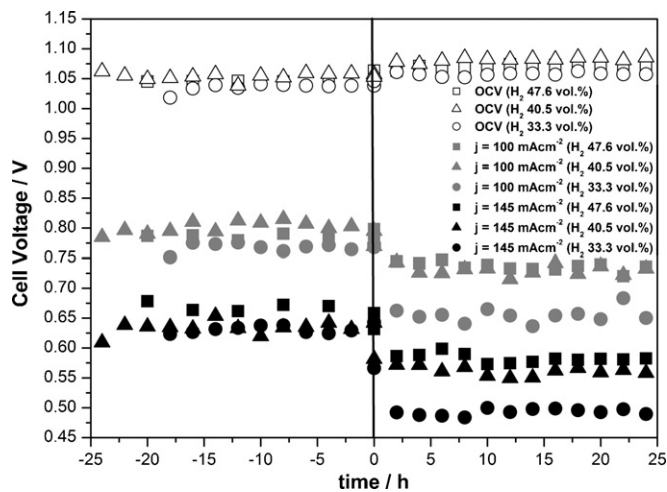


Fig. 8. Cell voltage evolution time for cells fed with anode gas containing 95 ppm of H_2S and different amount of H_2 . Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%, $40.5:54.7:4.8$ vol% and $33.3:61.9:4.8$ vol%.

pressure to hydrogen sulfide pressure ratio [22]. The second reason is that the electrochemical deposition of nickel sulfides depends on the competition between hydrogen in the anodic gas and sulfide anions dissolved in the electrolyte. Plotting cell voltage drop at 100 mA cm^{-2} as function of hydrogen concentrations, Fig. 9, it is evident a liner dependence with each other, as expected from Eq. (20), because the current generated by hydrogen discharge is directly proportional to available hydrogen.

Water effects on the recovering capability of cell performances are shown in Figs. 10 and 11. In particular, Fig. 10 shows cell voltage drops evolution time before, during and after poisoning with 95 ppm of H_2S . Recovering is conducted at the beginning with dry clean gas, but with humidified clean gas at the ending.

With a dry clean gas, it was observed just a negligible recovering effect because of two competitive reaction types with opposite effects. One type is the anode desulfuration induced by hydrogen in anodic gas, reverse reactions (15) and (17). The other one is the anode sulfuration induced by residual sulfide anions, dissolved in electrolyte yet, reaction (18).

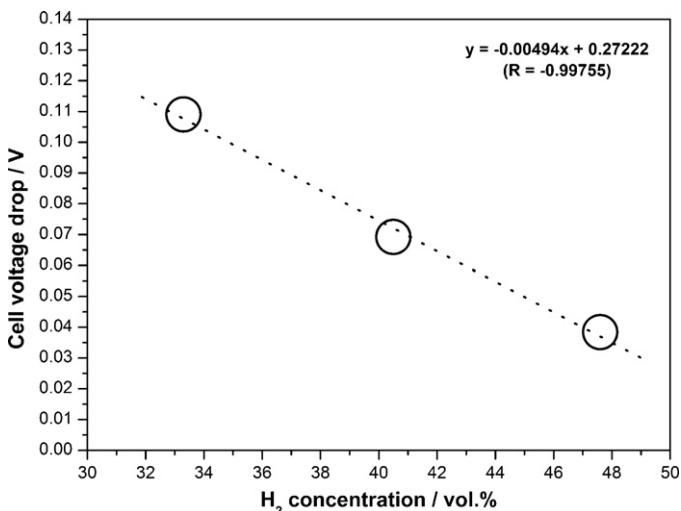


Fig. 9. Cell voltage drop as function of hydrogen concentrations for cells fed with anode gas containing 95 ppm of H_2S and under an applied load of 100 mA cm^{-2} . Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%, $40.5:54.7:4.8$ vol% and $33.3:61.9:4.8$ vol%.

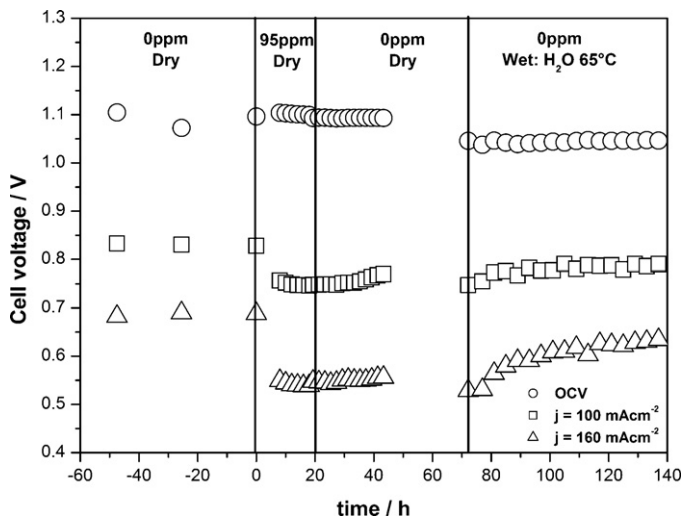


Fig. 10. Cell voltage evolution time before, during and after poisoning with 95 ppm of H_2S . Recovering is undertaken at the beginning with dry anode clean gas and finally with wet anode clean gas. Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%.

Vice versa, with humidified anode clean gas, cell performances are almost totally recovered because of two reaction types with synergic effects. One type is the anode desulfuration induced by hydrogen in anodic gas, reverse reactions (15) and (17). The other one is the electrolyte desulfuration induced by water in anodic gas, reverse reaction (9).

Fig. 11 shows cell voltage drops evolution time before, during and after poisoning with 95 ppm of hydrogen sulfide. Recovering is conducted with two humidified clean gases containing two different water vapor amounts. Different moisture levels are obtained setting two different temperatures (65°C and 75°C) for the humidifier. It was observed that high water amounts promote cell performances recovering because the electrolyte desulfuration, reverse reaction (9), is favored.

But actually, recovering is never complete. Irreversible sulfur poisoning effects are due to thermodynamically stable nickel sulfides formation.

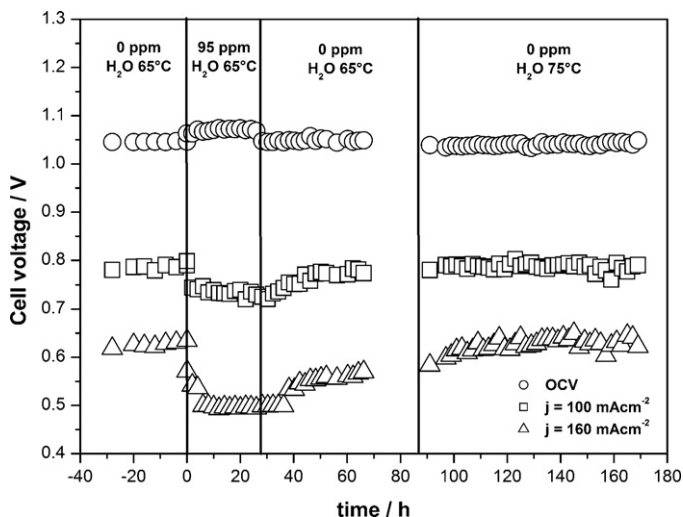


Fig. 11. Cell voltage evolution time before, during and after poisoning with 95 ppm of H_2S . Recovering is undertaken with two wet anode clean gas containing different water vapor amounts. Cell operating conditions: temperature 650°C ; pressure 1 atm; cathode gas $\text{O}_2:\text{N}_2:\text{CO}_2 = 14.41:54.22:31.37$ vol%; anode gas $\text{H}_2:\text{N}_2:\text{CO}_2 = 47.6:47.6:4.8$ vol%.

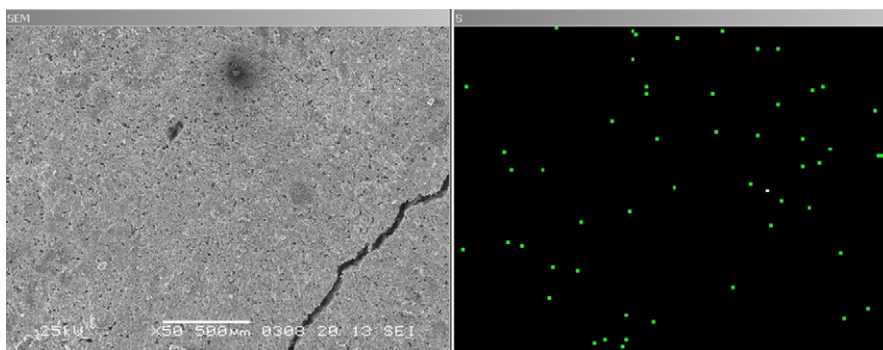


Fig. 12. Post-test SEM-EDX analysis of an anode poisoned with different hydrogen sulfide amounts (2, 26 and 95 ppm) and recovered with wet clean anode gas: (a) anode surface enlargement; (b) mapping of elemental sulfur on anode surface.

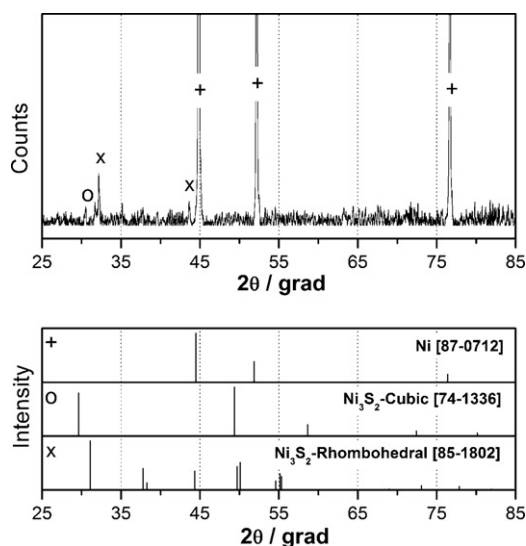


Fig. 13. XRD analysis of an anode poisoned with different hydrogen sulfide amounts (2, 26 and 95 ppm) and recovered with wet clean anode gas.

Figs. 12 and 13 show respectively scanning electrode microscopy (SEM) analysis and X-ray diffraction (XRD) analysis of an anode which was poisoned with different hydrogen sulfide amounts and subsequently recovered with clean anode gas containing high water vapor amounts. SEM-EDX analysis detects residual sulfur compounds on the anode surface and XRD analysis shows that the chemical composition of these compounds is Ni_3S_2 ,

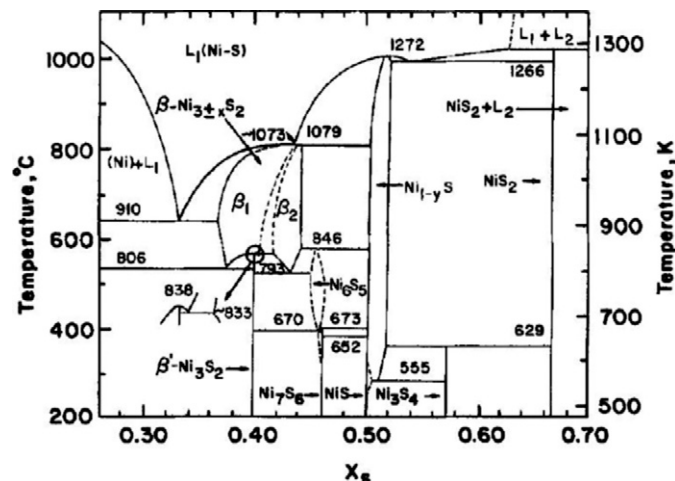


Fig. 14. Phase diagram of nickel-sulfur binary system.

as expected from phase diagram of nickel-sulfur binary system [23], Fig. 14.

5. Selection criteria

Experimental results drive us to claim that the performances decay for MCFC, fed with anode gas containing H_2S , is principally due to nickel sulfide formations via an electrochemical mechanism. Therefore, selection criteria for sulfur resistance anode materials have to be able to value both chemical and electrochemical parameters. In fact, anodes have to be made of materials whose chemical reactions with hydrogen sulfide are thermodynamically forbidden ($\Delta G > 0$) and electrode potentials for sulfides formation have such values that the anode degradation via electrochemical reactions is forbidden at cell operating conditions, typically 150 mA cm^{-2} .

One useful experimental parameter for evaluating the sulfur tolerance of anode materials, is the proportionality constant A in Eq. (20), which is related to the maximum effect of hydrogen sulfide on cell performances. The value of this parameter is empirically obtainable graphing cell voltage drops as function of H_2S concentrations for cells which are under a definite load current, Fig. 4.

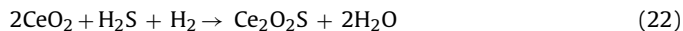
6. Alternative anodes

Currently we have been studying three types of anode materials which are resistance against hydrogen sulfide poisoning: NiAl; NiCr covered with CeO_2 ; NiCr covered with $\text{CeO}_2\text{-ZrO}_2$.

The first material, NiAl, is constituted by an electrocatalyst which is more resistance against hydrogen sulfide corruptions than conventional electrocatalyst, NiCr [24].

The second and the third materials are composed with the conventional electrocatalyst, NiCr, covered with a material acting as an easily recovering hydrogen sulfide trap, such as CeO_2 and $\text{CeO}_2\text{-ZrO}_2$ [15,25].

Ceria has such redox properties that it easily entraps hydrogen sulfide by reaction (22).



However, ceria-zirconia solid solutions have redox properties more useful than pure ceria. Its redox properties are modifiable by changing Ce/Zr ratio and thermal treatments used during solid solutions preparation. Also, adding ZrO_2 to CeO_2 increases the sintering resistance and promotes anode recovering for high oxygen storage capacity.

7. Conclusions

A 100 cm^2 class MCFC bench-scale single cell testing was used in this work. Sulfur poisoning levels depend on magnitudes of anode

surface area, as expected from Eq. (20). However, it does not compromise the investigation on sulfur poisoning mechanisms.

Hydrogen sulfide content in biogas for fuel cell affects MCFC performances because it reacts both with the anode and with the electrolyte. Poisoning effects occur via different mechanisms such as bulk chemical reactions, surface chemical reactions, surface physical actions and electrochemical reactions.

At low H₂S levels just two poisoning reaction types occur: physical and chemical absorptions on nickel surface by reactions (16) and (17); replacement of carbonate ions with sulfide and sulfate ions by reactions (9), (10), (11) and (12). In fact, formations of bulk nickel sulfides by reaction (15) are thermodynamically forbidden. However when it is applied a current at the cell, the anodic potential increases up to right values for nickel sulfide formations via electrochemical mechanisms, reaction (18). It means that under current load MCFC is more sensible to hydrogen sulfide attack.

Poisoning levels depend on applied current, hydrogen sulfide concentrations and hydrogen concentrations. While, cell performances recovery levels depend on water vapor amounts in inlet anode gas.

Irreversible poisoning effects are due to stable nickel sulfide formations, Ni₃S₂.

Selection criteria for alternative anode materials with a high resistance to hydrogen sulfide corrosion have to include evaluations of both thermochemical parameters such as Gibbs free energy of sulfuration reactions and electrochemical parameters such as electrode potential for sulfide depositions. One useful experimental parameter for evaluating the corrosion resistance is the proportionality constant *A* in Eq. (20), which it is possible to obtain graphing the cell voltage drop as function of H₂S concentrations.

Proposed anode materials include two different categories: anodes made of an electrocatalyst and a hydrogen sulfide trap such as NiCr covered with either CeO₂ or CeO₂–ZrO₂; anodes made of a hydrogen sulfide resistance electrocatalyst such as NiAl.

Acknowledgement

The authors gratefully acknowledge the assistance of Mr. Amedeo Masci in ENEA for SEM-EDX analysis.

References

- [1] OECD/IEA, 2007.
- [2] FAO, Bioenergy, Food Security and Sustainability-Towards an International Framework, High-Level Conference on World Food Security: The Climate Change and Bioenergy HLC/08/INF/3, June 3–8, 2008, Rome, 2008.
- [3] P. McKendry, *Bioresour. Technol.* 83 (2002) 37–46.
- [4] P. McKendry, *Bioresour. Technol.* 83 (2002) 47–54.
- [5] B.A. Peppley, *Int. J. Green Energy* 3 (2006) 201–218.
- [6] T. Kivisaari, P. Björnbohm, C. Sylwan, *J. Power Sources* 104 (2002) 115–124.
- [7] J. Xuan, M.K.H. Leung, D.Y.C. Leung, M. Ni, A review of biomass-derived fuel processors for fuel cell systems, *Renew. Sust. Energy Rev.* 13 (2009) 1301–1313.
- [8] K. Sasaki, *J. Fuel Cell Sci. Technol.* 5 (2008) 1–8.
- [9] T. Watanabe, Y. Izaki, Y. Mugikura, H. Morita, M. Yoshikawa, M. Kawase, F. Yoshida, K. Asano, *J. Power Sources* 160 (2006) 868–871.
- [10] A.F. Sammells, S.B. Nicholson, P.G.P. Ang, *J. Electrochem. Soc.* 127 (2) (1980) 350–357.
- [11] M. Kawase, Y. Mugikura, T. Watanabe, *J. Electrochem. Soc.* 147 (4) (2000) 1240–1244.
- [12] I. Uchida, S. Ohuchi, T. Nishina, *J. Electroanal. Chem.* 369 (1994) 161–168.
- [13] E.J. Vidt, G. Jablonski, J.R. Hamm, M.A. Alvin, R.A. Wenglarz, B. Patel, Evaluation of gasification and gas cleanup process for use in molten carbonate fuel cell power plants, Report DOE/MC/16220-1306 (1982), OSTI Identifier DE83003821.
- [14] M. Gong, X. Liu, J. Trembly, C. Johnson, *J. Power Sources* 168 (2007) 289–298.
- [15] H. Devianto, S.P. Yoon, S.W. Nam, J. Han, T.-H. Lim, *J. Power Sources* 159 (2006) 1147–1152.
- [16] Z. Cheng, S. Zha, M. Liu, *J. Electrochem. Soc.* 153 (7) (2006) A1302–A1309.
- [17] D. Weaver, J. Winnick, *J. Electrochem. Soc.* 136 (6) (1989) 1679–1686.
- [18] D. Townley, J. Winnick, H.S. Huang, *J. Electrochem. Soc.* 125 (5) (1980) 1104–1106.
- [19] L.G. Marianowski, G.L. Anderson, E.H. Camara, Use of sulfur containing fuel in molten carbonate fuel cells, U.S. Patent, No. 5,071,718 (1991).
- [20] J. Dong, Z. Cheng, S. Zha, M. Liu, *J. Power Sources* 156 (2006) 461–465.
- [21] W.M. Vogel, S.W. Smith, *J. Electrochem. Soc.* 29 (7) (1982) 1441–1445.
- [22] I. Alstrup, R. Rostrup-Nielsen, S. Roen, *Appl. Catal.* 1 (1981) 303–314.
- [23] R.Y. Lin, D.C. Hu, Y.A. Chang, *Metall. Trans.* 9B (1978) 531.
- [24] M. Farber, D.M. Ehrenberg, *J. Electrochem. Soc.* 99 (10) (1952) 427–434.
- [25] K.B. Yi, E.J. Podlaha, D.P. Harrison, *Ind. Eng. Chem. Res.* 44 (2005) 7086–7091.