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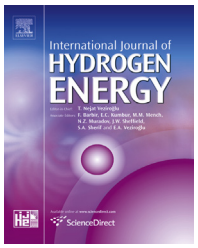

Experimental investigation of SO_2 poisoning in a Molten Carbonate Fuel Cell operating in CCS configuration

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ABSTRACT

One of the most interesting innovations in the CCS (Carbon Capture and Storage) field is the use of MCFCs as carbon dioxide concentrators, feeding their cathode side (or air side) with the exhaust gas of a traditional power plant. The feasibility of this kind of application depends on the resistance of the MCFC to air-side contaminants, with particular attention to SO_2. The aim of this work is to investigate the effects of poisoning when sulphur dioxide is added to the cathodic stream in various concentrations and in different operating conditions. This study was carried out operating single cells (80 cm^2) with a cathodic feeding composition simulating typical flue gas conditions, i.e. N_2, H_2O, O_2 and CO_2 in 73:9:12:6 mol ratio as reference mixture. On the anodic side a base composition was chosen with H_2, CO_2 and H_2O in 64:16:20 mol ratio. Starting from these reference mixtures, the effect of single species on cell poisoning was experimentally investigated considering, as main parameters chosen for the sensitivity analysis, SO_2 (0–24 ppm) and CO_2 (4–12%) content in the cathodic feeding mixture, H_2 (40–64%) content in the anodic stream as well as the operating temperature (620–680 °C). Results showed that degradation caused by SO_2 poisoning is strongly affected by the operating conditions. Data gathered during this experimental campaign will be used in a future work to model the poisoning mechanisms through the definition of MCFC electrochemical kinetics which take into account the SO_2 effects.

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Introduction

Recently the public awareness concerning greenhouse gases emissions, with particular reference to CO_2, has significantly increased.

It seems clear that the problem of global warming caused by greenhouse gases has to be tackled using a plurality of solutions and technologies to obtain results in short, medium and long term periods. In this scenario Carbon Capture and Storage (CCS) appears to be a suitable "bridge" technology in the transition to a low carbon economy. CCS, in fact, contributes to reducing atmospheric emissions coming from fossil fuel power plants, giving the needed time to renewable sources to reach an appropriate technology readiness level, in order to be a profitable alternative from economical and technical point of view.

Thanks to the reactions occurring at anode and cathode (reactions 1, 2), the MCFC can be considered a CO_2 concentrator. It transfers diluted CO_2 present at the cathode side to the anode side, where it is highly concentrated in a stream composed of just CO_2, H_2O and a small amount of unreacted fuel; thus CO_2 is easily separable from the anodic outlet.

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 \quad (1)$$

$$CO_2 + \frac{1}{2}O_2 + 2e^- \rightarrow CO_3^{2-} \quad (2)$$

The MCFC thus behaves as an *active* CCS technology, *producing* electric power (instead of consuming it in the case of passive technologies as ammine scrubbing) while removing carbon dioxide from the exhaust gases of traditional power plants.

Such post-combustion carbon dioxide separation is most effective applied to coal combustion and combined cycle power generation, due to the large potential of CO_2 reduction from these plants. The flue gas from these types of combustion technologies typically contains 3–12% CO_2 and residual O_2, both in the lower operational range of the MCFC: the stability of operation in these conditions has been studied experimentally in Refs. [1–8]. Several other studies have assessed the integration of an MCFC as CCS retrofit approaching the topic with numerical models, considering the same ranges of CO_2 content [9–13].

However, the greatest barrier to the feasibility of this application is the presence of pollutants in the flue gas entering the cathode. In CCS, SO_2 is the most harmful pollutant agent present in the flue gas, which causes performance decay and structural degradation of the MCFC. It is known that SO_2 content can significantly affect the cell performance as discussed in previous works [14–16]. Specifically, in Ref. [14] long term tests allowed to investigate the evolution of the sulphur poisoning mechanism under fixed operating conditions and concentrations of the pollutant agent. To provide a complete framework, necessary to perform quantitative analysis of this phenomenon, investigation must be carried out to characterize the effect of the main operating parameters on SO_2 poisoning. The objective of the present work addresses extended and immediate sulphur dioxide poisoning effects and how these are affected by the variation of operating parameters as SO_2 (0–24 ppm) and CO_2 (4–12%) contents in the cathodic feeding mixture, H_2 (40–64%) content in the anodic stream, as well as the operating temperature (620–680 °C). All the obtained data of this in-depth sensitivity analysis will be used in a future work to validate a kinetic model of the MCFC which takes into account also the poisoning due to SO_2.

SO_2 effects

There are few literature contributions concerning the interactions between SO_2 and MCFC, since this poisoning mechanism has not been studied as intensely as that of other pollutants like H_2S. Consequently, it is not easy to predict the effects of sulphur dioxide during the life of a cell. It appears that reactions, occurring when SO_2 is fed to the cathode, involve directly the electrolyte.

$$CO_3^{2-} + SO_2 + \frac{1}{2}O_2 \rightarrow SO_4^{2-} + CO_2 \quad (3)$$

$$H_2S + CO_3^{2-} + 3H_2O \leftrightarrow SO_4^{2-} + CO_2 + 4H_2 \quad (4)$$

Specifically, SO_2 is converted to sulphate by reaction (3); consequently, under load, sulphate ions migrate to the anode, accumulating in the electrolyte. At the anode side sulphur is released as H_2S according to the reverse of reaction (4).

Beyond corrosion of metallic parts, sulphur causes poisoning both due to loss of CO_3^{2-} charge carriers in the electrolyte (3), as due to H_2S released from the electrolyte at the anode side.

The effects of hydrogen sulphide on MCFC components have been deeply investigated [17–23]. In particular, H_2S reacts:

- according with chemisorption (5) and adsorption (6) reactions [20], on the anode nickel surface

$$Ni_{(s)} + H_2S_{(g)} \rightarrow Ni - H_2S_{(ads)} \quad (5)$$

$$Ni_{(s)} + H_2S_{(g)} \rightarrow Ni - HS_{(ads)} + Ni - H_{(ads)} \rightarrow Ni - S_{(ads)} + Ni + H_{2(g)} \quad (6)$$

- chemically (7) and (8) [17]

$$Ni + H_2S \rightarrow NiS + H_2 \quad (7)$$

$$3Ni + xH_2S \rightarrow Ni_3S_X + xH_2 \quad (8)$$

- electrochemically (9) and (10) [17]

$$Ni + S^{2-} \rightarrow NiS + 2e^- \quad (9)$$

$$3Ni + xS^{2-} \rightarrow Ni_3S_X + 2xe^- \quad (10)$$

The effects of these reactions depend on chemical and electrochemical conditions, but all contribute to decreasing cell performance, forming nickel sulphides on the anode surface. The latter block active sites meant for hydrogen