

Open-circuit-potentials of gas/electrode/YSZ boundary versus molten carbonate reference electrode at medium temperatures

II. Potential response of Au, Pt and Ni-cermet electrodes in $\text{CH}_4 + \text{O}_2$ and $\text{H}_2 + \text{O}_2$ gas mixtures

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Abstract

Values of open-circuit-potentials (OCP) have been determined for pairs of electrodes: Au and Pt, Ni– $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ cermet and Au, Pt and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ composite at the YSZ electrolyte, in the uniform atmospheres of $x\text{CH}_4 + y\text{O}_2 + (1 - x - y)\text{Ar}$ gas mixtures with variable x and y coefficients, at 600 °C. The determined dependencies of OCP values on the initial gas mixture compositions have been compared with the respective dependencies calculated for equilibrium or *quasi*-equilibrium compositions of these gas mixtures. The OCP values for the pair of Pt and Au electrodes have been measured also in the $x\text{H}_2 + y\text{O}_2 + (1 - x - y)\text{Ar}$ uniform gas mixtures but no distinct difference of the OCP values has been observed in this atmosphere. For some pairs of electrodes investigated in $x\text{CH}_4 + y\text{O}_2 + (1 - x - y)\text{Ar}$ atmospheres the measured OCP values have shown differences up to ca 0.9–1.0 V. These differences were stable within large range of compositions of this gas mixture. Within this gas composition range one of the electrodes conserves the potential of oxygen electrode determined by oxygen partial pressure in the initial gas mixture and is insensitive to reaction occurring in the gas phase. These results are discussed on the basis of equilibria or some *quasi*-equilibria, that establish in the C–H–O gas mixture and the solid carbon deposition is considered. For a given pair of dissimilar electrodes, their selective sensibility to the electrochemical process of oxygen electrode has been confirmed. Within large range of gas mixture concentrations, in the Pt–Au electrode pair Au has shown behavior of the oxygen electrode, whereas the OCP values of the Pt electrode are within the range of hydrogen electrode, also at gas compositions corresponding to the solid carbon stability. With this pair the OCP differences of ca. 600 mV have been obtained. Among three electrodes studied the cermet Ni– $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrode shows the best electrocatalytic properties resulting in the OCP values following exactly the respective equilibrium dependence. In the pair Ni– $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ and Au a stable potential difference of ca. 900 mV have been established. Unexpectedly, Pt electrode in the pair with the $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ composite electrode plays role of the oxygen electrode quite insensitive to other components of the equilibrated initial gas mixture. This surprising fact seems indicate that in conditions of the experiments performed the electrocatalytic behavior of the electrode depends not only of the material of this electrode but also on the properties of the second electrode in the given pairs of electrodes.

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1. Introduction

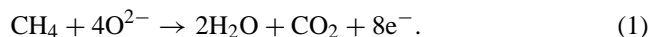
The concept of a fuel cell with two electrodes in the same uniform atmosphere of fuel + oxidant gas mixture (the single chamber fuel cell) has been formulated by few authors.

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First Eyraud et al. in 1961 have proved the existence of a potential difference between two electrodes of different materials deposited on the humid surface of γ -alumina layer in the uniform gas atmosphere. These authors have attributed this effect to the diffusion of ions on the solid electrolyte surface and have formulated a concept of a fuel cell on this basis [1]. Dyer has found that in the uniform atmosphere of $H_2 + O_2$ mixture two electrodes of the same metal—one at the surface of the solid ionic conductor, second placed inside of this material—show a noticeable difference of the open-circuit-potentials (OCP) [2]. This effect has been claimed characteristic for a very thin layer of solid conductor, permeable for both gases. Potential difference measured between two electrodes of dissimilar metals on a porous oxide substrate covered by an adsorbed moisture layer in air has been explained by the oxidation of metal at one electrode and the reduction of oxygen at the other [3]. In the last decade, in a series of articles Hibino and Iwahara have published the results of investigations regarding a cell with two electrodes of different materials in contact with a solid ionic electrolyte, working at high temperature and using gas mixtures of fuel composed of hydrocarbons with air (C–H–O gas mixtures) as energy source. They have proposed a novel solid oxide fuel cell system, which does not need to separate the supply of fuel and oxidant gases. These authors have proved that under the uniform gas atmosphere of methane and oxygen, Ni-cermet and Pt electrodes at the solid YSZ electrolyte may show a potential difference of ca. 0.7 V [4]. In the next investigation, this group of authors has described a Pt|BaCe_{0.8}Y_{0.2}O_{3- α} |Au cell, in which two electrodes were exposed to the same mixture of CH₄ and air [5]. With a pair of Pd and Au electrodes in contact with the above electrolyte an improved power density has been obtained [6]. By addition of MnO₂ to the YSZ electrolyte and to the pair of Pt and Au electrodes these authors have obtained even more promising voltage–current characteristics [7]. They have concluded that a contribution of electronic conductivity of both n- and p-types, resulting of doping the YSZ electrolyte by MnO₂ or TiO₂ or coating the YSZ surface with Pt₆O₁₁, respectively, increases the length of triple-phase-boundaries (TPBs) where electrode reactions take place. In a single-chamber-SOFC device with YSZ electrolyte, nickel anode and La_{0.8}Sr_{0.2}MnO₃ (LSM) cathode, supplied with a mixture of CH₄ + air 1:1 mixture at 950 °C, Hibino et al. have obtained the OCV values up to ca. 800 mV and power densities up to ca. 120 mW/cm². This performance has been improved by a simultaneous addition of Ce_{0.8}Gd_{0.2}O_{1.9} to the nickel anode and of MnO₂ to the LSM cathode, respectively, and was much better than that of the Pt|YSZ|Au cell [8]. Farther increasing of the power density delivered by this cell up to ca. 260 mV/cm² has been obtained by deposition of Mn, Gd, Cr, Ce and Lu oxides on the YSZ surface [9]. The concept of the single-chamber-SOFC has been developed up to the system of Ni–Ce_{0.8}Sm_{0.2}O_{1.9}(cermet)|La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃|Sm_{0.5}Sr_{0.5}CoO₃ where several C–H–O fuels (hydrocarbons and

LPG) mixed with air may deliver power within 450–650 °C temperature range [10].

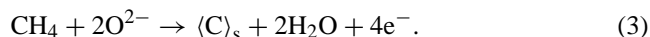
The authors of experimental works cited above have focused their attention rather on the practical than on chemical aspects of functioning of such systems. At the set out of the idea of a single-chamber-SOFC was the evidence of the irreversibility of at least one of the electrodes in such a cell. Riess et al. have proposed a simple thermodynamic theory of this cell, limited, however, to the case of the H₂ + O₂ mixture supplying two different electrodes [11]. At one of those electrodes the chemical equilibrium between the fuel and the oxidant must be easily established, whereas at the second electrode the rate of this process must be very slow. No doubts, that the power delivered in this cell has its origin in the different sensibility of the electrodes to the potential generating reactions. Taking into account the electrochemical character of the potential-generating equilibria at both electrodes one may believe, that at the electrode with a good electrocatalytic properties the fuel component of the gas mixture is anodically oxidized by the O²⁻ ions delivered by the solid electrolyte for example the process of the entire electrochemical oxidation of methane is



To the thermodynamic and kinetic behavior of this electrode the concepts regarding the mechanism of the direct anodic oxidation of C–H–O fuel at the electrode/solid electrolyte interface are applicable. For fuels containing compounds of carbon and hydrogen, the full oxidation process leads to H₂O and CO₂ formation. Hibino et al. [8] claimed that in the CH₄ + O₂ gas mixture supplying the single-chamber SOFC rather the process of a partial oxidation of methane takes place, according to



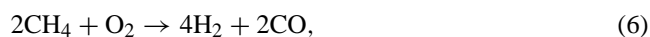
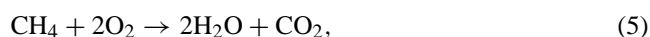
Occurring only of reaction (2) excludes CO₂ formation. On the other hand, one cannot neglect also a possible partial anodic oxidation process when only hydrogen produced by methane decomposition is oxidized and carbon is deposited as solid phase:



Oxygen ions consumed in electrochemical reactions (1), (2) and/or (3), must be reproduced on the other electrode according to the cathodic reaction:



However, in the CH₄ + O₂ gas mixture methane may be oxidized also in chemical reactions:



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