

PRODUCTION OF "GREEN NATURAL GAS" USING SOLID OXIDE ELECTROLYSIS CELLS (SOEC): STATUS OF TECHNOLOGY AND COSTS

M. Mogensen¹, S.H. Jensen¹, S.D. Ebbesen¹, A. Hauch¹, C. Graves¹, J. V. T. Høgh¹, X. Sun¹, S. Das¹, P.V. Hendriksen¹, J.U. Nielsen², A.H. Pedersen³, N. Christiansen², J.B. Hansen⁴

¹Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark (DTU), DK-4000 Roskilde, Denmark.

²Topsoe Fuel cell A/S, Nymøllevej 66, DK-2800 Lyngby, Denmark.

³DONG Energy A/S, Nesa Alle 1, DK-2820 Gentofte, Denmark

⁴Haldor Topsøe AS, Nymøllevej 55, DK-2800 Lyngby, Denmark

Introduction

Increasing the production of sustainable CO₂-neutral energy is of great importance because greenhouse gas emissions need to be reduced and because there may not be sufficient supplies of inexpensive oils and natural gas in the relative near future. Denmark's aim is to become independent of coal, oil and gas by 2050. Then it is natural to look for photosynthesis products (biomass) to replace fossil fuel, but there will not be enough biomass available to substitute the fossil fuels.

Another method of producing "green natural gas" or substitute natural gas (SNG) is via synthesis gas produced by electrolysis. This presentation gives a review of the state of the art (SOA) of co-electrolysis of a mixture of CO₂ and H₂O to produce syngas (CO + H₂) using high temperature solid oxide cells (SOCs), and includes some analysis of the potentials and challenges of producing gases like CH₄, (CH₃)₂O and higher hydrocarbons by catalytic conversion of the syngas. A brief description of the high pressure electrochemical laboratory at Risø National Laboratory is given as part of the SOA review.

Why SOEC?

The reversibility of the solid oxide fuel cell (SOFC), i.e. that it can also work in solid oxide electrolyser cell (SOEC) mode, was proven 30 years ago by A.O. Isenberg (Solid State Ionics, vol. 3-4, p. 431 (1981)). Electrolysis of steam into H₂ and of CO₂ into CO was demonstrated. Huge international R&D efforts on SOFC have improved the performance of this cell type tremendously since the work of Isenberg, and the state of the art is now approaching commercialization. This fact and the increasing concerns about fossil fuels have spurred renewed international interest in SOEC for production of syngas (H₂ + CO) by co-electrolysis of a mixture of CO₂ and H₂O. Subsequently, the syngas can be converted into various synthetic gases.

There are two main arguments in favor of the high temperature co-electrolysis: 1) electrolysis is an endothermic process that utilizes the unavoidable Joule heat of the electrochemical cell, i.e. the SOEC is a self cooling (thermoneutral) system; 2) the high temperature in the range of 700 - 900 °C yields fast kinetics.

Gas types

CH₄ (the main component of substitute or synthetic natural gas (SNG)), is the simplest hydrocarbon. If the electrolyser is pressurized CH₄ can to some extent be formed inside the electrolyser (around 10 % at 10 MPa in the range of 700 - 800 °C). Further conversion of the syngas into CH₄ will need integration into a system with a catalytic reactor running at much lower temperature in the range of 300 - 400 °C, which so far is below the practical lower limit for the operation temperature of an SOEC. Pressurized CH₄ may be fed into the natural gas (NG) pipeline network directly. Many countries including Denmark already have an existing finely distributed NG pipeline network. SNG is a superior energy carrier compared to

hydrogen, because CH_4 has an energy density about $3\frac{1}{2}$ times that of H_2 , and most pipeline steels do not tolerate pure pressurized hydrogen - they become brittle.

Another interesting possibility is the production of dimethyl ether (DME) using an SOEC and a catalytic reactor integrated together into single system. DME may directly substitute liquefied petroleum gas (LPG). We have modeled an integrated system that combines an SOEC and a catalytic syngas-to-DME reactor. The advantages and challenges in optimizing the system, e.g. how to reach the optimal ratio of $\text{CO}/\text{H}_2 = 1$ plus just a few percent of CO_2 and lowest possible content of steam, are analyzed in the presentation.

Results

Examples of the results obtained in the research conducted at Risø DTU and Topsøe are given as illustrations, e.g. pressurized cell tests have been carried out using furnaces placed inside room-temperature-autoclaves, see Figure 1. Further, co-electrolysis has been demonstrated at ambient pressure on a 1 kW cell stack level. Figure 2 shows results.

We also discuss the technical requirements of SOEC technology based on today's economic situation. It is shown that the SOC has a clear potential as an energy converter that can turn fluctuating renewable power into manageable synthetic hydrocarbons. The initial performance of the Risø - Topsoe SOEC is acceptably high already. The main obstacle for a fast commercialization is lifetime, which at the present state is too short at current densities (SNG production rates) higher than 10 kA m^{-2} (ca. $1 \text{ Nm}^3 \text{ h}^{-1} \text{ m}^{-2}$, in words 1 normal cubic meter of SNG per hour and square meter of cell). Below ca. 7 kA m^{-2} the durability of the Topsoe Fuel Cell stacks is good.

Further, co-electrolysis of CO_2 and steam in biogas can be used for the upgrading of biogas to make it suitable for storage and transport using the NG network. This requires a special treatment or special type of electrodes as well as high pressure operation. A new Danish project exploring this possibility has just been started and initial experimental results are expected ready for presentation at the conference.

Outlook

The R&D that still remains in order to obtain a commercially viable SOEC converter will be outlined based on our own studies of performance and degradation. SOA of cost calculations and projections will also be presented.



Figure 1. Photo of three autoclaves at Risø DTU for testing solid oxide cells up to $1000 \text{ }^\circ\text{C}$ and up to 10 MPa (1 of them) and 5 MPa .

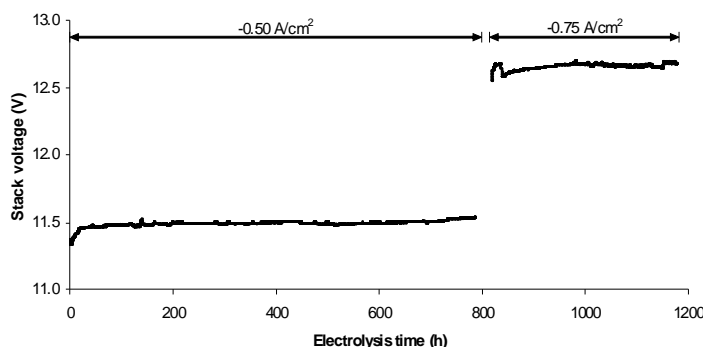


Figure 2. Voltage as a function of time for co-electrolysis of H_2O and CO_2 in a 1 kW (10 cell) stack with a foot print of $12 \times 12 \text{ cm}^2$ showing good durability.