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State of the art in high-temperature electrolysis and research trends

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Abstract:
A promising method for hydrogen production is high-temperature electrolysis. Here, the energy for water splitting can be applied by electricity and heat, in contrast to the well-established low-temperature electrolysis processes, where only electricity can be used. In this article the working principle, active materials, and the fundamental thermodynamics of high-temperature electrolysis are described. Furthermore an overview is given of material research, system optimization, and degradation investigations. In these fields progress is needed to lead the high-temperature electrolysis to a commercial application.

Anotace:
Vysokoteplotní elektrolýza je nadějná metoda pro výrobu vodíku. V tomto procesu je možné nahradit část energie potřebné pro štěpení vody teplem v protikladu od dobře známých nízkoteplotních elektrolytických metod, kde lze použít pouze elektrickou energii. V tomto článku je vylíčen funkční princip, aktivní materiály a základní termodynamika vysokoteplotní elektrolýzy. Kromě toho je zde podán přehled výzkumu v oblastech keramických materiálů, optimalizace systémů a příčin a průběhu degradace. V těchto oborech je nezbytný pokrok pro zavedení této technologie na trh.

ÚVOD

In the future energy supply it is assumed that hydrogen will play an important role. An often-cited possible application of hydrogen is the energy storage to match supply and demand when using renewable intermitting energy sources. Another application area is transport, due to the vast occurrence of hydrogen on earth. As hydrogen, however, appears only in compounds it must be produced by splitting these bonds. One method for generation of hydrogen is water electrolysis. Compared to the well-established technologies of low-temperature alkaline or polymer electrolysis, high-temperature electrolysis is still in research [1], [2]. However, the high-temperature electrolysis offers the advantage that part of the energy for the chemical bond splitting can be supplied by heat. This reduces the need of electrical energy and raises the efficiency. It also allows the combining with other high-temperature processes and to use waste heat.

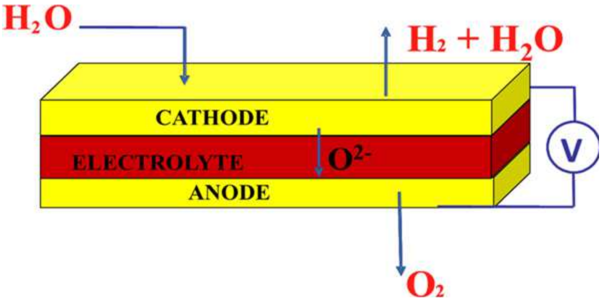
FUNDAMENTALS

Working principle

Figure/obrázek 1 shows a high-temperature electrolysis cell (SOEC). It consists of three active ceramic layers. At the cathode water is split into hydrogen and oxygen ions, equation 1, oxygen ions then migrate through the electrolyte to the anode and are there recombined with electrons to oxygen gas, equation 2. The overall reaction of water splitting is given by equation 5.

$$H_2O + 2e^- \rightarrow H_2(g) + O^{2-} \qquad (1)$$

$$O^{2-} \rightarrow 1/2O_2(g) + 2e^- \qquad (2)$$



Obr. 1: Scheme and working principle of a high-temperature electrolysis cell [3]

Materials for SOEC

The material for the *air side electrode* has to fulfil the following requirements: electrical and anionic conductivity, porosity for gas transport, chemically stable in oxidizing atmosphere, heat resistant, and compatible with the thermal expansion coefficient of the electrolyte material. Perovskite materials of ABO_3 type are generally used [4]. The most typical air side electrode material is $LaMnO_3$, doped with Sr.

The *electrolyte* material has to possess only ionic conductivity, has to be gas tight, and compatible to the thermal expansion coefficients of both electrodes. The main material categories for the electrolyte are partially cation-substituted ZrO_2, CeO_2, $LaGaO_3$ and apatites. Typically used is ZrO_2 stabilized with 8mol% Yttrium, so-called YSZ.

The specifications for the *fuel side electrode* are electrical and ionic conductivity, porosity for gas transport, chemically stable in reducing atmosphere, heat resistance, and compatibility of thermal expansion coefficient with adjacent layers. These requirements fulfils a mixture of electrolyte material with nickel, most frequently employed is Ni-YSZ.

When talking about SOEC (solid oxide electrolysis cell), also the concept of proton conducting electrolyte should be mentioned. In this case, the reactions 3 and 4 take place in the electrodes. The following perovskites have been used as an electrolyte in proton conducting cells: $BaCeO_3$, $BaZrO_3$, $SrCeO_3$, $LnWO_{12}$, and $LnNbO_4$ [5], [6], [7], and [8]. The material choices for air side and fuel side electrode stay unchanged compared to oxygen ion conducting cells. The main advantage of this concept is that hydrogen is produced undiluted at the cathode.

$$H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^- \qquad (3)$$

$$2H^+ + 2e^- \rightarrow H_2(g) \qquad (4)$$

Thermodynamics

The free enthalpy ΔG of the equation 5 is the minimum electrical energy that is necessary for electrolysis. As can be seen in fig./obr. 2, ΔG decreases with increasing temperature. The remaining energy demand, $T\Delta S$, can be provided by heat. If this heat can be delivered from an external process, the costs for hydrogen production can be reduced significantly.

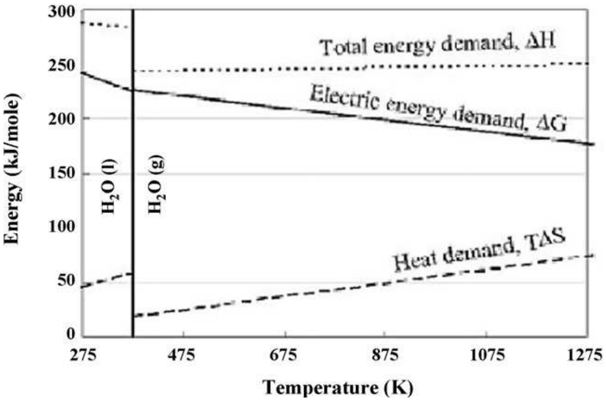
$$H_2O \rightarrow H_2(g) + 1/2O_2(g) \qquad (5)$$

RESEARCH TRENDS

The overall aim is to reduce the costs of a SOEC stack to approx. 500 €/kW [9] and to prolong lifetime. This can be achieved by material optimization, design improvements, and minimization of degradation.

Material optimization and design

In material optimization the research object is to enhance electrical properties of the active materials. This does not only mean the optimization of materials, but it also includes the optimizing of manufacturing processes. The search for new materials is important, too. But as Tietz et al. point out in [10], this is a very complex procedure because not only the properties of the new component have to be investigated, but also its effects on the whole cell, and a well-adapted and reproducible manufacturing process needs to be developed.



Obr. 2: Thermodynamics of water electrolysis [3]

Improvement and development of cell and stack design

Mainly the sealing is a difficult issue in high-temperature technologies. Therefore the aim is to find and test suitable sealing materials, to reduce sealing area or to transfer it to colder areas. Well known is the concept of Hexis, where no sealing in the hot zone is needed [11]. Also a very interesting design was developed Saint-Gobain set up on research from the research centre Jülich [12], [13]. Five cells are connected to a stack with ceramic interconnectors. This block is easy to handle.

The conception of a single chamber fuel cell is characterized by having only one gas chamber. The working principle is based on the difference in catalytic activity of the electrodes for the anodic and cathodic reactions, respectively [14].

The dual cell concept combines SOFC (solid oxide fuel cell) and SOEC by adding a proton and oxygen ion conducting high temperature cell [15].

The examples of HEXIS and single-chamber fuel cell concept have been used as SOFCs only until now.

Degradation investigation of cell and stack components

The lifetime performance of high-temperature cells is still not satisfying. Degradation phenomena and overview is giving in [16] and [17]. In [18] it is also mentioned that in SOEC mode have occurred specific degradation mechanisms, which are not known for SOFCs. Degradation is difficult to investigate due to two reasons. On the one hand, degradation depends on various parameters like for example current density, steam content in the fuel gas, steam conversion rate, and temperature, and on the other hand the tests are very time consuming. The longest SOEC test over 9000h is reported by Tietz et al. [18]. One the longest SOFC stack test over 19000 h describe Malzbender et al. [19]. A whole system was tested for almost 17000 h by Siemens Westinghouse [20].

PROJECTS IN ŘEŽ

Centrum Výzkumu Řež (CVŘ)

Within the European research project SUSEN [21] an experimental facility for hydrogen production by high-temperature water electrolysis is under construction. This includes equipment for manufacturing and testing SOFC and SOEC. The facilities will be available for research activities from universities as well as companies.

Ústav jaderného výzkumu (UJV)

UJV also deals with high-temperature electrolysis [22], other projects cover different hydrogen technologies: operation of a hydrogen bus and a hydrogen filling station [23], planning and building a power supply system for a single-family home including photovoltaic panels and alkaline electrolysis [24].

CONCLUSIONS

High-temperature electrolysis has the potential for highly efficient systems. This is the reason so many research institutes deal with this topic. But as described above there is still a lot of work necessary to reduce costs and increase lifetime performance of cells and systems.

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