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Electrocatalysts for the generation of hydrogen, oxygen and synthesis gas

Foteini M. Sapountzi [a,*], Jose M. Gracia [b], C.J. (Kees-Jan) Weststrate [a], Hans O.A. Fredriksson [a], J.W. (Hans) Niemantsverdriet [a,b]

[a] SynCat@DIFFER, Syngaschem BV, P.O. Box 6336, 5600 HH Eindhoven, The Netherlands
[b] Syncat@Beijing, Synfuels China Technology Co. Ltd, 1 Leyuan 2 South Street, Section C, Yanqi Economic Development Area, Beijing 101407, China

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ABSTRACT

Water electrolysis is the most promising method for efficient production of high purity hydrogen (and oxygen), while the required power input for the electrolysis process can be provided by renewable sources (e.g. solar or wind). The thus produced hydrogen can be used either directly as a fuel or as a reducing agent in chemical processes, such as in Fischer–Tropsch synthesis. Water splitting can be realized both at low temperatures (typically below 100 °C) and at high temperatures (steam water electrolysis at 500–1000 °C), while different ionic agents can be electrochemically transferred during the electrolysis process (OH^-, H^+, O^{2-}). Singular requirements apply in each of the electrolysis technologies (alkaline, polymer electrolyte membrane and solid oxide electrolysis) for ensuring high electrocatalytic activity and long-term stability. The aim of the present article is to provide a brief overview on the effect of the nature and structure of the catalyst–electrode materials on the electrolyzer's performance. Past findings and recent progress in the development of efficient anode and cathode materials appropriate for large-scale water electrolysis are presented. The current trends, limitations and perspectives for future developments are summarized for the diverse electrolysis technologies of water splitting, while the case of CO_2/H_2O co-electrolysis (for synthesis gas production) is also discussed.

Contents

* Corresponding author. Syngaschem BV, P.O. Box 6336, 5600 HH Eindhoven, The Netherlands.
E-mail address: foteini@syngaschem.com (F.M. Sapountzi).

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1. Hydrogen: potential energy carrier, clean fuel, valuable chemical and essential ingredient of synthesis gas

The increase in world's energy consumption during the last decades is a result both of the global rise in population and of the changes in the standards of living [1]. Indicatively, the average global power demand is predicted to be approximately 30 and 46 TW in 2050 and 2100 respectively [2]. Nowadays fossil fuels (i.e. coal, oil, natural gas) constitute the primary source that covers global energy needs. The continuously increasing energy demands, the limiting reserves of fossil fuels together with the environmental and societal problems created by the fossil fuel dependence (e.g. global warming, acid rain, local air quality deterioration) render an urgent need for the development of new energy strategies with limited greenhouse gas emissions. These will rely both on renewable energy sources (which are more abundant and cleaner compared to fossil fuels) and on chemical processes for synthetic fuel production (e.g. Fischer–Tropsch synthesis) [1–6].

A fundamental problem related with the use of solar and wind energies is their inability to operate independently from demand, since their unscheduled intermittent supply often mismatches the grid power demands. Thus, the development and application of systems for the efficient storage of excess electricity is entailed [7,8]. Electrocatalytic technologies can play a crucial role for the indirect storage of surplus renewable energy via the conversion of electricity to chemical energy [8]. Among them, water electrolysis is a promising alternative compared to electricity storage using batteries [9]. During water electrolysis, renewable energy can be used as the electricity source to split water into hydrogen and oxygen. The thus produced green hydrogen can be either stored and used in the chemical industry or used for electricity generation (through fuel cells or internal combustion engines) with zero post-combustion pollutants [6].

The use of hydrogen as an energy carrier has a number of advantages. Hydrogen (a) is relatively abundant in nature (in water) [1] and can be produced using either renewable or non-renewable sources [10], (b) can be used as a fuel in both fuel cells and internal combustion engines (the latter however suffers from concomitant NO_x production) [8], (c) has high gravimetric energy density i.e. up to three times larger than liquid hydrocarbon–based fuels [4,11] (however worth to note is its low volumetric energy density which caused safety issues with its pressurized storage), (d) has small environmental footprint, since the only product of its oxidation is water [6,8]. Its use in the transport sector has been successfully introduced and Hua et al. recently reviewed the status of hydrogen-fueled buses in Europe, USA and Canada [12].

However, using hydrogen as a fuel requires appropriate infrastructures and huge investments. A more feasible scenario for tackling the energy problem concerns the employment of water electrolysis for the production of synthetic fuels that can be used in the current infrastructures. Renewable energy sources will provide the electrons required for the splitting of water. In a parallel process, CO_2 will be captured from large point sources and be recycled with the utilization of the renewably produced hydrogen (reverse water–gas-shift reaction) for the production of synthetic fuels (Fischer–Tropsch synthesis) [13]. Additionally, hydrogen can be also used as a reducing agent of several other catalytic processes in the petroleum and chemical industry, e.g. for the refining and upgrading of crude oil and for ammonia synthesis respectively [1].

In 2015, the worldwide hydrogen production is around 50 Mt per year [1,8,10,13–16] and is covered by fossil fuels (steam reforming of natural gas, coal gasification, partial oxidation of hydrocarbons) [1,8,10,15,16]; however, this includes the concomitant production of CO_2. Within the vision for a sustainable future, several methods, other than water electrolysis, for renewable hydrogen production have been developed, such as biomass gasification, thermochemical water splitting and photoelectrochemical water splitting [10,15]. Among them, water electrolysis is the only mature technology that is currently commercially available [15].

Hydrogen production via electrolysis using renewable energy sources amounts to only 4% of today's hydrogen production, mainly due to economic factors (i.e. lack of widely available renewable energy systems of low cost, high capital cost, high energy input required) [10]. This picture is going to change in the near future and increase in the use of renewable energy sources is expected, since the European Energy Directive has set the target for covering 14% of the energy needs by renewable energy sources by 2020. Hydrogen production by water electrolysis using renewable energy sources is expected to play a key role in the scenario of a green energy economy [8]. Clear advantages of this method is the high efficiency and the high purity of the produced hydrogen, which is of great importance for its subsequent conversion to electricity using low temperature polymer electrolyte fuel cells [17]. Furthermore, high purity oxygen is a valuable by-product of water electrolysis. Its utilization both in medical care and in chemical industry (blast furnaces, electric furnaces and glass melting, gasification) could lead to substantial decrease in the nominal cost of water electrolysis [18].

2. Water electrolysis technologies

Depending on the kind of electrolyte and thus the type of ionic agent (OH^-, H^+, O^{2-}), and the operation temperature, water electrolyzers are classified into three main categories: alkaline [19], polymer–electrolyte membrane (PEM) [20,21] and solid oxide electrolyzers (SOE) [22–24]. The operating principles of the three main types of electrolysis technologies are presented in Fig. 1.

Solid oxide electrolyzers (SOEs) operate typically at temperatures above 500 °C, with water in the form of steam. The SOE