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Sustainable generation of hydrogen using chemicals with regional oversupply – Feasibility of the electrolysis in acido-alkaline reactor

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ABSTRACT

An integral part of the concept of sustainable development and a serious challenge to be addressed is the demanding and costly disposal of the hazardous waste chemicals and/or overproduced chemicals remaining after various production cycles in the chemical industry. For example, the recently reported overproduction of sulfuric acid in China can affect base metal production rates. In this context the consideration of new technologies that can avoid environmental damage or even introduce an economically feasible framework for the utilization of hazardous waste chemicals becomes appealing.

In this work, adopting the fundamental aspects of electrochemical thermodynamics, for the first time the feasibility of efficient hydrogen production in an acido-alkaline electrochemical cell is analyzed. Generation of hydrogen, based on the utilization of low cost ("cost-free") acids/bases whose world turnover is measured in tens and hundreds of megatons, and importantly, who suffer from regional overproduction, is proposed. The cell with two electrolytes separated by the cation transparent membrane is proven to be operational at significantly lower voltage than conventional water electrolysis cell, as long as cathodic reaction proceeds in acidic while anodic reaction proceeds in alkaline media. Significant electric energy saving, in comparison to conventional water electrolysis can be of high impact taking into consideration the general tendency of growing electricity price. While the economic justification of this particular concept has to be carefully examined considering the local conditions and technical implementation, acido-alkaline electrochemical cells are recognized as feasible and can have a distinct role for sustainable energy conversion and storage and waste utilization.

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Introduction

Besides challenges induced by the increasing global energy demand, one of the central constraints for the sustainable development are environmental concerns related to the disposal of hazardous waste chemicals [1,2]. One of the difficulties the global chemical industry is facing is how to deal effectively with regional oversupply caused by the local overproduction of chemicals [3]. For several years, already, the increasing production of glycerol in Brazil, which is a by-product of biodiesel production, has been perceived as an issue of serious concern [4]. While overproduction of glycerol in Brazil has implications for one particular country, in some other cases overproduction and its consequences are already global phenomena. Certainly very important is the predicted tremendous growth in the production of sulfuric acid. Specifically, the production of sulfuric acid is the most important method for removing sulfur oxides from copper, lead and zinc smelter gases [5]. The increasing production of copper, lead and zinc, together with the necessity of meeting emission standards [6,7] causes the expansion of the contact acid plants for removal of sulfur from the smelter. Recently reported sulfuric acid oversupply in China [8] shows that the overproduction of this side product can actually impact base metal smelter production rates. One of the solutions for the neutralization of sulfuric acid is its disposal as gypsum ($CaSO_4$), which requires limestone or lime as a neutralization agent. Despite the minor applications of gypsum it is predominantly disposed of as a solid waste [5]. Therefore, a qualitatively different approach for the neutralization of excess sulfuric acid, that still contains significant chemical energy, would be more beneficial. A similar challenge is met in the production processes where bases occur as a side product, as for instance in the chlor-alkali industry. Since the ratio of the major products is fixed, this results in *ca.* 1.13 tons of NaOH accompanying each ton of generated chlorine. Since markets do not consider the laws of stoichiometry, chlor-alkali industry is in a state of perpetual imbalance and either chlorine or caustic soda is in long supply, while there is a shortage of the other. This situation is reflected in spot market prices that can fluctuate widely over short periods [9], driven for instance by the overproduction of NaOH in India [10] and in the Middle East [11] as has recently been reported. In order to maintain and cover the market demand, the producers are indirectly forced to cause continuously overproduction of some of the chemicals. This is witnessed by data from a few years ago show that while global demand in NaOH reached 51 Mton, its supply was around 60 Mton [12].

In this context, it is particularly important to design new technologies, which do not harm the environment and/or can utilize hazardous waste chemicals, especially if waste chemicals can be used for obtaining clean and environmentally friendly energy carriers. Considering that the global electric power demand is at least 16 TW and that 87% of the energy supply comes predominantly from fossil fuels [2], replacement of conventional fuels with renewable and alternative energy sources is of mayor importance. Particularly demanding is the storage of electrical energy originating from renewable sources (for example, wind energy). An area of intensive research for decades has been the so called hydrogen economy [13,14], where hydrogen is considered to be the main medium for energy storage. Nowadays, industrially relevant amounts of hydrogen are predominantly obtained from fossil fuels using steam reforming, a widespread, but unsustainable method due to the concomitant CO and CO_2 release. A reasonable alternative to steam reforming is the electrochemical approach for hydrogen production by water electrolysis using renewable electricity as a sustainable low temperature process. Alternatively, it is also produced as a side product in chlor-alkali technology. While during water electrolysis both redox reactions typically happen in the same electrolyte, in a chlor-alkali reactor the electrolytes operate at two markedly different pH values [9]. Namely, in this process chlorine is anodically generated in acidic media (pH around 2) while hydrogen is cathodically generated in alkaline media (pH above 14). Historically, this was the first acido-alkaline electrochemical cell with technical importance. Today it is the one of the essential (electro)chemical technologies with the turnover in tens of megatons output [15]. The success of chlor-alkali technology also gave the impetus for the current work. Although such acido-alkaline reactors can be considered as a proven technology on large as well as on small scale, only a few literature reports can be found to date. To the best of our knowledge only acido-alkaline fuel cell for the generation of electricity [16] and acido-alkaline redox flow battery have been reported previously [17]. Neither any publically available work could be found on the process of utilizing

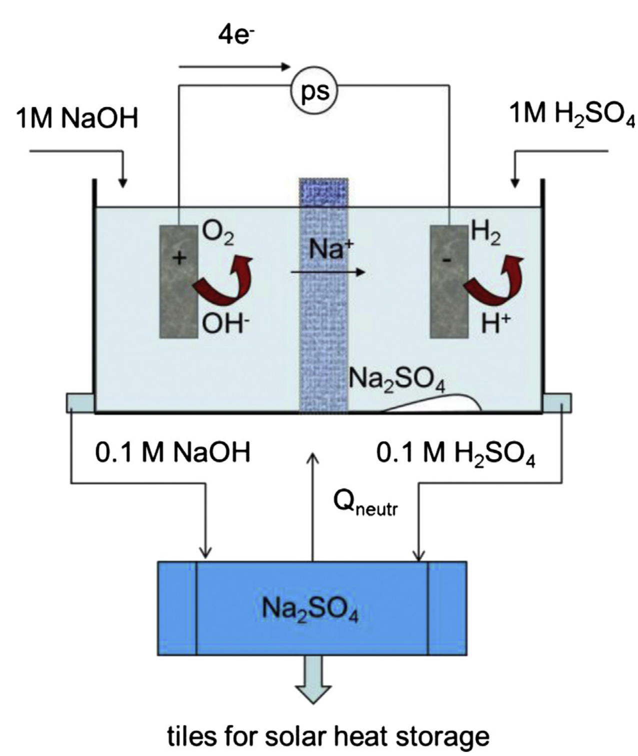

Fig. 1 – Scheme illustration of an acido-alkaline electrochemical cell for the hydrogen and oxygen production.