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Progress of international program on hydrogen production with the copper–chlorine cycle

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ABSTRACT

This paper highlights and discusses the recent advances in thermochemical hydrogen production with the copper–chlorine (Cu–Cl) cycle. Extended operation of HCl/CuCl electrolysis is achieved, and its performance assessment is conducted. Advances in the development of improved electrodes are presented for various electrode materials. Experimental studies for a 300 cm^2 electrolytic cell show a stable current density and production at 98% of the theoretical hydrogen production rate. Long term testing of the electrolyzer for over 1600 h also shows a stable cell voltage. Different systems to address integration challenges are also examined for the integration of electrolysis/hydrolysis and thermolysis/electrolysis processes. New results from experiments for $CuCl–HCl–H_2O$ and $CuCl_2–HCl–H_2O$ ternary systems are presented along with solubility data for CuCl in HCl $–H_2O$ mixtures between 298 and 363 K. A parametric study of multi-generation energy systems incorporating the Cu–Cl cycle is presented with an overall energy efficiency as high as 57% and exergy efficiency of hydrogen production up to 90%.

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1. Introduction

Utilization of hydrogen as a clean energy carrier is a promising alternative to conventional fossil fuels. Sustainable, lower cost, and "green" methods of hydrogen production are needed to adopt hydrogen on a wider scale. Usage of hydrogen has the potential to significantly reduce the emissions of greenhouse gases that contribute to climate change, if produced using renewable energy sources. This is one of the reasons why hydrogen is often cited as a future energy carrier that can become a significant contributing factor to sustainable energy supply [1], as well as a prominent fuel.

Large-scale sustainable methods of hydrogen production require an energy source such as nuclear or solar energy. For large-scale capacities of hydrogen production, thermal energy can be supplied by nuclear reactors. Electrolysis is a commercially available technology that uses electricity for water splitting and hydrogen production. Thermochemical cycles are promising water splitting alternatives that can be linked with nuclear reactors to thermally decompose water into oxygen and hydrogen, through a series of intermediate reactions. The Cu–Cl cycle is a hybrid thermochemical cycle, including both electrochemical and thermal steps. This paper outlines recent advances in thermochemical hydrogen production with the Cu–Cl cycle.

The copper-chlorine (Cu -Cl) cycle is a promising cycle for hydrogen production by thermochemical water decomposition due to its lower temperature requirement and better overall efficiency than other thermochemical cycles [2–4]. The Cu–Cl cycle consists of a closed loop of thermally driven chemical reactions, where water is decomposed into hydrogen and oxygen, and all other intermediate compounds are recycled with no emissions to the environment [2,3,5]. This paper focuses on the four step Cu–Cl cycle for hydrogen production as described in Fig. 1. The four reactions of the Cu–Cl cycle are:

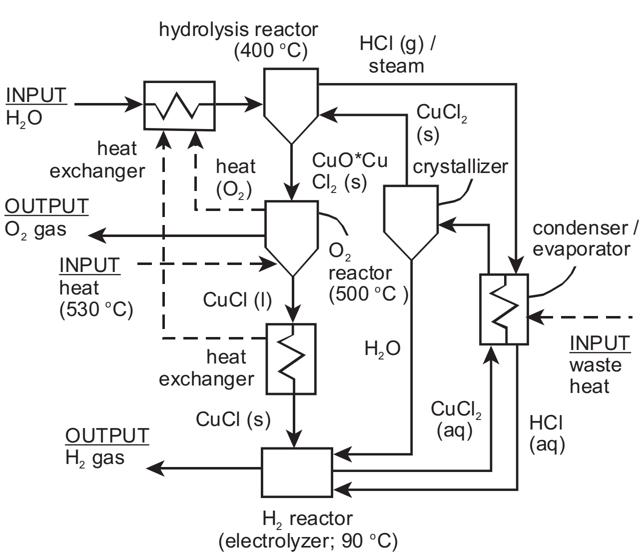

Fig. 1 – Schematic of the thermochemical copper–chlorine cycle.

$$2CuCl_{(aq)} + 2HCl_{(aq)} \rightarrow 2CuCl_{2(aq)} + H_{2(g)}(\text{electrochemical})\text{ at } 25\text{–}90\ ^\circ C;\ \text{step (1)} \quad (1)$$

$$2CuCl_{2(aq)} \rightarrow 2\ CuCl_{2(s)}(\text{physical})\text{ at } 60\text{–}200\ ^\circ C;\ \text{step (2)} \quad (2)$$

$$2CuCl_{2(s)} + H_2O_{(g)} \leftrightarrow Cu_2OCl_{2(s)} + 2HCl_{(g)}(\text{hydrolysis})\text{ at } 350\text{–}450\ ^\circ C;\ \text{step (3)} \quad (3)$$

$$Cu_2OCl_{2(s)} \rightarrow 2CuCl_{(l)} + \tfrac{1}{2}\ O_{2(g)}(\text{thermolysis})\text{ at } 520\ ^\circ C;\ \text{step (4)} \quad (4)$$

In comparison to other thermochemical cycles, the Cu–Cl cycle has the advantage of an ability to utilize low-grade waste or process heat to achieve higher thermal efficiency and lower cost of hydrogen production than other technologies [6–8]. The Cu–Cl cycle has a reduced electrical power requirement, compared to typical water electrolysis, for its CuCl/HCl electrolysis. The $CuCl_2$ hydrolysis reaction and Cu_2OCl_2 thermolysis reaction form a closed loop with the CuCl/HCl electrolyzer to produce hydrogen in the cycle. In the hydrolysis reactor, the chemical conversion effectiveness decreases as reactants are consumed [9]. Past studies on the conversion extent of the solid hydrolysis reactant indicated an optimal conversion of 4 mol–15 mol of steam per mol of HCl produced [10]. Experimental data [11] and thermodynamic analysis [12,13] suggest an optimal temperature of the hydrolysis reactor to be approximately 375 °C. Lewis et al. [14] examined the conversion extent in the CuCl/HCl electrolyzer. In the Cu_2OCl_2 thermolysis reactor, a conversion extent of 85% was reported [14]. In this paper, the integration of the electrolyzer and hydrolysis reactor in the Cu–Cl cycle is reported in terms of energy and mass flows. A crystallization process is also reported to reduce the quantity of H_2O entering the hydrolysis reactor.

Past studies have successfully demonstrated the unit operations of each of the processes of the Cu–Cl cycle [15,16]. Few studies have examined the integration of reactions and interaction between processes. The hydrolysis process and its integration with electrolysis entail significant challenges. These include the excess steam requirement of the hydrolysis reaction above the stoichiometric amount to obtain >95% yield of Cu_2OCl_2. The concentration of the produced HCl in the hydrolysis reaction is not sufficient to meet the minimum requirement of the electrolysis reaction. Increasing the steam to $CuCl_2$ ratio only further reduces the concentration of HCl. The operating temperature of the hydrolysis and electrolysis reactions differs significantly, requiring a substantial heat exchange to condense the high temperature effluent and reheat the products for subsequent processes in the cycle [10,15,17].

Recent results of analysis of the integration of the hydrolysis and electrolysis steps were reported by Sayeed et al. [16]. Results of the kinetics in the hydrolysis reactor indicate that excess steam is required in the hydrolysis reactor, which subsequently reduces the overall efficiency of the Cu–Cl cycle. The adverse effects of excess steam on the cycle efficiency were reduced by using a heat recovery steam generator (HRSG)