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Electrochemical analysis of a HCl(aq)/CuCl(aq) electrolyzer: Equilibrium thermodynamics

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ABSTRACT

A CuCl electro-thermochemical process is a promising hydrogen production method, in part because among other thermochemical cycles as it requires low heat temperatures and also almost half the electrical power of water electrolysis. A CuCl(aq)/HCl(aq) electrolyzer forms the electrochemical part of process and is examined in this work. This study uses equilibrium thermodynamics as a tool to improve understanding of the behavior of anodic and cathodic half reactions as well as the full cell at equilibrium conditions. The results are reported on variation of decomposition potentials of the hydrogen evolution reaction at the cathode and four probable redox reactions on anode surface by temperature and also degree of conversion of Cu(I) species to Cu(II) species at the anode. The term “Gibbs conversion coefficient” is proposed for the typically used term “thermodynamic efficiency” for the redox reactions. The Gibbs conversion coefficients of the redox reactions are studied as temperature varies for different Cu(I) to Cu(II) conversions. All anode half-reactions trigger at the same specific potential. However, depending on the concentrations of active species, only one reaction is dominant. In addition, as conversion begins at the anode, the required decomposition potential increases sharply, then continues to rise steadily at a slower rate. At 25 °C the magnitude of the full-cell electrolysis decomposition potential is 0.40 V at 5% conversion of the anolyte, while at 80 °C the corresponding value rises to 0.44 V. The Gibbs conversion coefficients of the full-cell reaction at 25 °C and 80 °C are obtained as approximately 22% and 80%, respectively.

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Introduction

The copper-chlorine (Cu–Cl) thermochemical cycle has been receiving significant attention as a potential hydrogen production method (compared to current processes like steam methane reforming) for several reasons, including moderate working temperature (around 550 °C), lower complexity, inexpensive chemicals and high efficiency [1]. Actually, over

200 thermochemical water decomposition processes [2] are known as important hydrogen production technologies for future in large scales [3]. The most important advantage of these thermochemical cycles is zero greenhouse gas emission process whereby chemical reactions through a closed internal loop recycle all chemicals continuously [4]. An example of scaled up equipment is sulfur–iodine cycle pilot plant by Japan Atomic Energy Agency that produced approximately 30 l/h hydrogen [5]. Research centers worldwide work on

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Nomenclature

A	Theoretical constant of Debye–Huckel parameter, $\text{mol}^{-0.5} \text{kg}^{0.5}$
a	Activity of ion
\dot{a}	Common ion diameter, Å
b	Input amount of element, mol
B	Theoretical constant of Debye–Huckel parameter, $\text{mol}^{-0.5} \text{kg}^{0.5}$
C	Empirical-extended parameter of third approximation of Debye–Huckel theory
c	Concentration of ion, mol l^{-1}
E	Potential, V
F	Faraday constant, C mol^{-1}
\bar{g}	Specific molar Gibbs free energy, mol l^{-1}
\bar{h}	Specific molar enthalpy, mol l^{-1}
I	Ionic strength of electrolyte
k	Rate constant of reaction, $\mu\text{mol s}^{-1}$
m	Number of existing phases
Q	Heat, J
z	Number of exchanged electrons

Greek letters

α	Symmetry factor or transfer coefficient
γ	Activity coefficient of ion
ε	Gibbs conversion coefficient
θ	Dielectric constant
Λ	Pre-exponential factor
ϕ	Lagrangian factor
$\bar{\mu}$	Molar chemical potential, J mol^{-1}
σ	Membrane ionic conductivity, S cm^{-1}
Φ	Stoichiometric number of element
Ψ	Efficiency

Subscripts

C	Current
Cell	Electrolyzer full-cell
D	Decomposition
DH	Debye–Huckel
e	Electrolyte
HER	Hydrogen evolution reaction
Heat	Heat
i	ith ion
j	jth phase
Ox	Oxidant
P	Products
R	Reactants
r	Reaction
S	Setchenow coefficient
1	Reaction 1
2	Reaction 2
3	Reaction 3
4	Reaction 4

Superscripts

$^{\circ}$	Standard condition
N	Stoichiometric number of species

developing other cycles as: iron-chlorine (Fe–Cl), copper-sulfate (Cu–So₄), cerium-chlorine (Ce–Cl), vanadium-chlorine (V–Cl), the hybrid chlorine [6], and copper-chlorine (Cu–Cl) cycle [7] that were identified as the most promising cycles in a Nuclear Hydrogen initiative [8]. Taking into account integration of the above mentioned cycles with the Generation IV SCWR (Super-Critical Water Cooled Reactor), a lower temperature requirement (around 550 °C) of Cu–Cl cycle makes it outstanding compared to 800 °C or higher temperature demands by other proven cycles that is out of capability of Generation IV reactors [9]. Other advantages for Cu–Cl cycle are lower construction material demand, common chemical agents, reactions going to full completion, and low electrolyzer cell required applied potential [6].

Canada as the leader of the Cu–Cl cycle project has put effort to develop an integrated large lab-scale demonstration equipment [6] through the Generation IV International Forum (GIF) [10]. The Canadian-led team consists of University of Ontario Institute of technology (UOIT), University of Toronto, University of Guelph, University of Western Ontario, University of Waterloo, UNENE (University Network of Excellence in Nuclear Engineering), and Atomic Energy of Canada Limited (AECL) as Canadian collaborators and Argonne National Laboratory (ANL), and Pennsylvania State University (PSU) as U.S. members. Each of named members focuses on some particular aspects of project with UOIT as the place to demonstrate and develop unit operations. In future, all unit operations will be integrated to a whole cycle at UOIT which will be the final step of large-scale pilot cycle development project. Started from 2009 couple of progress report papers have been published by all members [3,4,6,8,9, and 11] where developments have been reported on unit facilities, material selection, cycle simulation for integration feasibility analysis, heat recovery, experimental unit operations, safety aspects and etc.

Regarding the electrochemical step (electrolysis) of the Cu–Cl cycle parallel to other parts, numerous works have been carried out especially by UOIT, AECL, ANL, and PSU. Initially AECL demonstrated feasibility of hydrogen production by the Cu–Cl electrolyzer continuously for several days [8,9] as result two patents have been published by AECL for Cu–Cl electrolyzer development in 2010 [12] and 2015 [13]. They reported that electrolysis is feasible at considerably low potentials (0.6–0.7 V) at a current density of 0.1 A cm^{-2} using inexpensive materials [3,9]. Also AECL has done comprehensive studies for material selection for electrolyzer cell through material degradation analysis [14]. In US work has been focused on proper membrane development to reduce copper crossover from anode to cathode which is considered as a poison for cell [11]. Intent is to identify a type of membrane with same proton conductivity but with copper crossover rates. Detail data on comparative study of studied membranes can be found in Ref. [6]. At PSU they have done electrolyzer efficiency assessments using Nafion 117 membranes. Adding to this, they have published couple of informative papers on electrochemical study of half-cell reactions and also anolyte speciation analysis plus full cell performance determination [15–23]. PSU works especially [20,22] filled many gaps in

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