Electrolysis of CuCl in HCl medium

Venus Chaudhary[a] , Ashwini B. Nirukhe[b], Damaraju Parvatalu[b], Ganapati D. Yadav[a*]
[a]Department of Chemical Engineering, Institute of Chemical Technology, Matunga (E), Mumbai-400019, Maharashtra, India
[b]ONGC Energy Centre, ONGC complex, IEOT, Phase II, Panvel, Navi Mumbai- 410221, Maharashtra, India
*gd.yadav@ictmumbai.edu.in

Abstract:

Electrolysis of CuCl for generation of copper powder and cupric chloride is one of the critical steps in the Copper-Chlorine cycle used for hydrogen production. In the electrolysis reaction, CuCl dissolved in dilute HCl solution is oxidized to $CuCl_2$ at the anode and reduced to copper at the cathode. Major challenge of this process is to achieve high current density and high current efficiency during the electrolysis of CuCl. Thus, a study on these aspects is essential for successful implementation of reaction in the Cu-Cl cycle. This paper represents investigation of effect of operating parameters upon scaleup of the electrochemical cell using the Mixed Metal Oxide (MMO) coated on titanium mesh as anode. Studies on current-voltage characteristics, effect of variation of flow rate and effect of concentration of electrolyte were carried out in HCl medium. After experiments, titrations, weight of electrodeposited copper, SEM, particle size analysis were done to calculate the current density and current efficiency. The study showed improvement in current efficiencies and copper deposition rate. SEM analysis of copper revealed dendritic gr owth of copper.

Keywords: Copper-Chlorine cycle, Electrolysis of CuCl, Mixed Metal Oxide, Current Efficiency

Introduction

The growing energy demand has led to exploitation of fossil fuels. This has not only led to depletion of the fossil fuel reserves but also has contributed to greenhouse gas (mainly CO_2) emissions. Reducing the dependence on fossil fuels and minimizing harmful environmental impact can be achieved by sustainable energy sources derived from renewables. Production of sustainable hydrogen using water splitting is one such clean and green approach. Hydrogen as energy carrier is an emerging area of research and of future importance. Various technologies are advancing for hydrogen production for large scale applications. Technological developments in water splitting for production of hydrogen using intermediates is progressing rapidly. Copper-chlorine cycle for water splitting is one of the most promising method for hydrogen production. Extensive research is carried out worldwide on Cu-Cl cycle by Argonne National Laboratory (ANL), Atomic Energy of Canada Limited (AECL), University of Ontario Institute of Technology (UOIT), etc. In India, ONGC Energy Centre (OEC) in collaboration with Institute of Chemical Technology, Mumbai (ICT) has developed and patented a novel breakthrough zero-discharge process for water splitting using Cu-Cl route (ICT-OEC Cu-Cl cycle). One of the crucial steps of ICT-OEC Cu-Cl cycle is electrolysis of CuCl. The present paper presents and discusses the importance of parameters for CuCl electrolysis in HCl medium in the Cu-Cl cycle leading to copper generation at cathode and cupric chloride at anode, separated by a membrane at room temperature.

PROCESS

The ICT-OEC Cu-Cl cycle [1] is a patented zero-discharge closed loop multistep process where all the chemicals are recirculated and reused. The resulting net reaction is water splitting to hydrogen and oxygen. The cycle consists of four thermochemical reactions, one electrochemical reaction and one unit operation (drying). Electrochemical reaction consists of electrolysis of CuCl to produce Cu at cathode and $CuCl_2$ at anode. The produced Cu and $CuCl_2$ then acts as reactants for hydrogen generation step and hydrolysis/decomposition step (through drying) as shown in fig 1. The electrolysis of CuCl is thus an integral part of ICT-OEC Cu-Cl cycle for hydrogen production using water splitting.

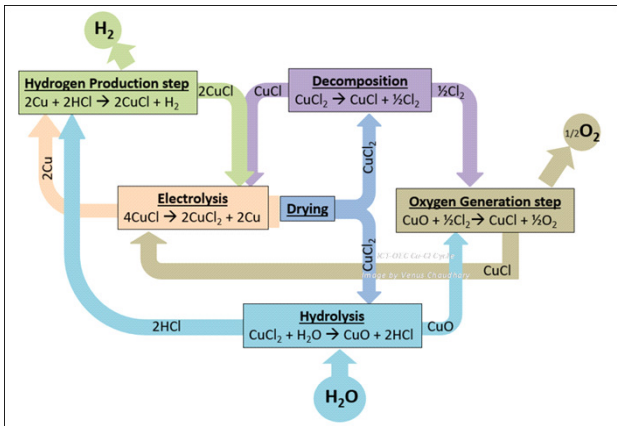


Fig 1: Schematic of ICT-OEC Cu-Cl cycle

ANL in collaboration with AECL initiated the development of an electrolytic cell using single compartment cells for disproportionation of CuCl in an aqueous system to produce copper at a cell voltage 0.4-0.8 V for this closed cycle. Gas Technology Institute (GTI) developed an electrolytic cell where anode and cathode compartments were separated by anion exchange membrane [2]. AECL, UOIT, GTI and Pennsylvania State University are developing the CuCl/HCl electrolyzer to produce H_2 [3, 4] and studying the feasibility of solid platinum, glassy carbon electrodes, ceramic carbon electrode (CCE). One of the challenges of electrolysis of CuCl is to achieve a good current density and efficiency [2]. Also, use of pure platinum as anode is of concern due to the high costs involved.

Literature reported so far is mainly focused on using platinum, graphite and carbon-based materials as electrodes. Also, the current density remains a challenge. The experimental studies by Atomic Energy of Canada Limited (AECL) at 0.4 to 0.8V using graphite electrodes with 0.3M CuCl in 4M HCl resulted in current density of 29 to 37 mA/cm^2. Another study by AECL at 0.5V to 0.8V using Pt anode and Cu cathode with 0.3N CuCl in 4M HCl reveals current density as 14 to 86 mA/cm^2 [6-8]. The experimental studies at the Argonne National Laboratory (ANL) demonstrated current density of 21 mA/cm^2 at 0.4V and 135 mA/cm^2 at 0.6V with 0-4M HCl and 0.03-0.3N CuCl [6, 9]. The studies also revealed that the current efficiency is more than 95% when the cell potential is stable at 0.7 V, and the current density is 0.5 A/cm^2 for a 36h test using a customized Nafion based membrane [4]. Another study at ANL demonstrated that Nafion-based and porous polyethylene (PPE) membranes can inhibit copper transport with HCl as a catholyte [10]. Sathaiyan et al. [11] have studied electrolysis of CuCl-HCl with 1M CuCl anolyte and 6M HCl catholyte for the generation of hydrogen gas at 70°C at normal atmospheric pressure using a plain graphite anode and 0.30 mg/cm^2 platinum plated graphite cathode and using nafion cation exchange membrane-32. Cathodic current density of 250 A/m^2 was obtained. Khurana et al. [12] have operated the CuCl electrolyzer for 168 h at 0.3 A/cm^2 under 0.7 V. The study was conducted at 80°C and the solutions were pumped at a flow rate of 130 ml/min with a constant current density of 0.3 A/cm^2 for 168 h. Santhanam and Easton [13] have reported the reaction rate for Cu(I) oxidation three times faster on a Pt electrode compared to a carbon surface. Ranganathan and Easton [14] have reported a new CCE structure based on poly aminopropyl siloxane (PAPS) that vastly outperformed a traditional carbon fibre paper (CFP) electrode.

Considering above developments, the preliminary studies on increasing the current density and efficiency using alternative anodic material were initiated. This paper represents further investigations of CuCl electrolysis studies using MMO as an alternative to platinum and subsequent investigation of operating parameters

such as voltage, flowrate and electrolyte concentration.

EXPERIMENTAL WORK

Electrochemical setup

The electrochemical system was fabricated as per [15] with in-house facilities using acrylic as MOC for cell. An anion-exchange membrane, Snowpure® Excellion was used to separate anodic and cathodic compartments. Mixed Metal Oxide (MMO) coated on Ti-mesh was used as anode and copper rod was used as cathode. Peristaltic pumps were used for recirculation of electrolyte during the reaction. The electrolyte was prepared by dissolving CuCl in HCl medium. A DC power supply with output voltage 0-2V and current rating 0-60A was used to provide the required voltage and to note the output current in the electrochemical system. The electrochemical system is outline in fig 2.

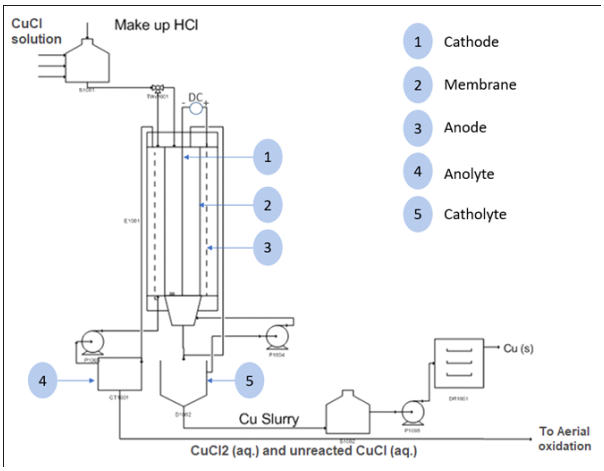


Fig 2: Electrochemical system for CuCl electrolysis

Methodology

Studies on current-voltage characteristics, effect of variation of flow rate and effect of concentration of electrolyte were carried out. Initially, experiments on current voltage characteristics were carried out with parameters as 0.3N CuCl, 3N HCl and 7mm dia. copper rod. During these experiments, the voltage was gradually increased from 0.3V to 2.1V and the output current was noted for both the systems; platinum sheet as well as MMO coated on Ti-Mesh as anode. Thereafter, studies on variation of flowrate were carried out to determine its effect on the current density and efficiency with parameters as 0.3N CuCl, 3N HCl, 7mm dia. copper rod and 1V. The flow rate ratio of recirculation of anolyte to catholyte was varied as 1, 1.25, 1.5, 1.75, 2 and 2.25. Furthermore, experiments with increased CuCl concentration in feed (0.5N) were carried out. During these studies, the HCl concentration was adjusted such that the CuCl gets completely solubilized (3.5N HCl and 4N HCl).

The CuCl and $CuCl_2$ concentrations at anode and cathode side before and after reaction were determined by oxidation with potassium iodate and iodometric titrations respectively. The copper powder deposited on cathode was washed with water to remove the residual CuCl/HCl and was oven dried to remove the moisture. Characterization of copper powder was done using Scanning Electron Microscopy (SEM) and Particle Size Analyzer.

Calculations

The current efficiencies are calculated using the formulae as follows:

$$\text{Cathodic current efficiency} = \frac{\text{Amount of Cu formed in cathode side}}{\text{Theoretical amount of Cu formed by Faraday law}}$$

$$\text{Anodic current efficiency} = \frac{\text{Amount of } CuCl_2 \text{ formed in anode side by electrolysis reaction}}{\text{Theoretical amount of } CuCl_2 \text{ formed by Faraday law}}$$

RESULTS

Preliminary studies of MMO coated Ti-mesh and Pt as anode

Studies on Current Voltage characteristics revealed that the MMO coated on Ti mesh performed better than platinum sheet. The difference in output current was significant at voltage above 0.9V as shown in fig 3 indicating better performance at higher voltage.

Effect of variation of flowrate

It was observed that as the flowrate ratio of anolyte recirculation to catholyte recirculation was

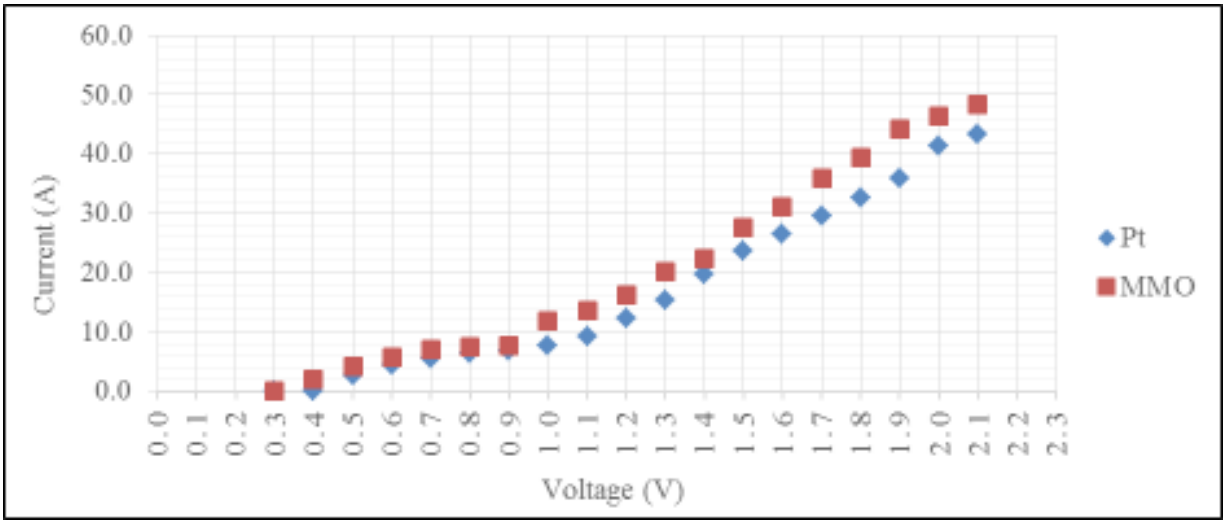


Fig 3: Current Voltage Characteristics of Pt and MMO in electrolysis of CuCl

increased, the electrolysis reaction was enhanced as outlined in fig 4. With increase in flowrate ratio from 1 to 2, the maximum cathodic density was found to be increased from 108 mA/cm^2 to 126 mA/cm^2. Accordingly, the cathodic current efficiency and anodic current efficiency also increased from 94% and 86% to 109% and 107% respectively. Subsequently, the copper deposition rate at cathode improved from 22.8g/h to 23.6g/h and the concentration of $CuCl_2$ formed at anode side increased from 0.278N to 0.298N; approaching the theoretical value of 0.3N. This may be due to the increase in the flow across the membrane particularly at the anodic side resulting in higher mass transfer. After further increasing the flowrate ratio to 2.25, the maximum cathodic current density and copper deposition rate increased to 131 mA/cm^2 and 26.1g/h but cathodic and anodic current efficiencies obtained were 98% and 101% respectively.

Effect of concentration of electrolyte

As the concentration of electrolyte was increased to 0.5N CuCl, the current efficiencies were enhanced as expected. HCl medium of 4N

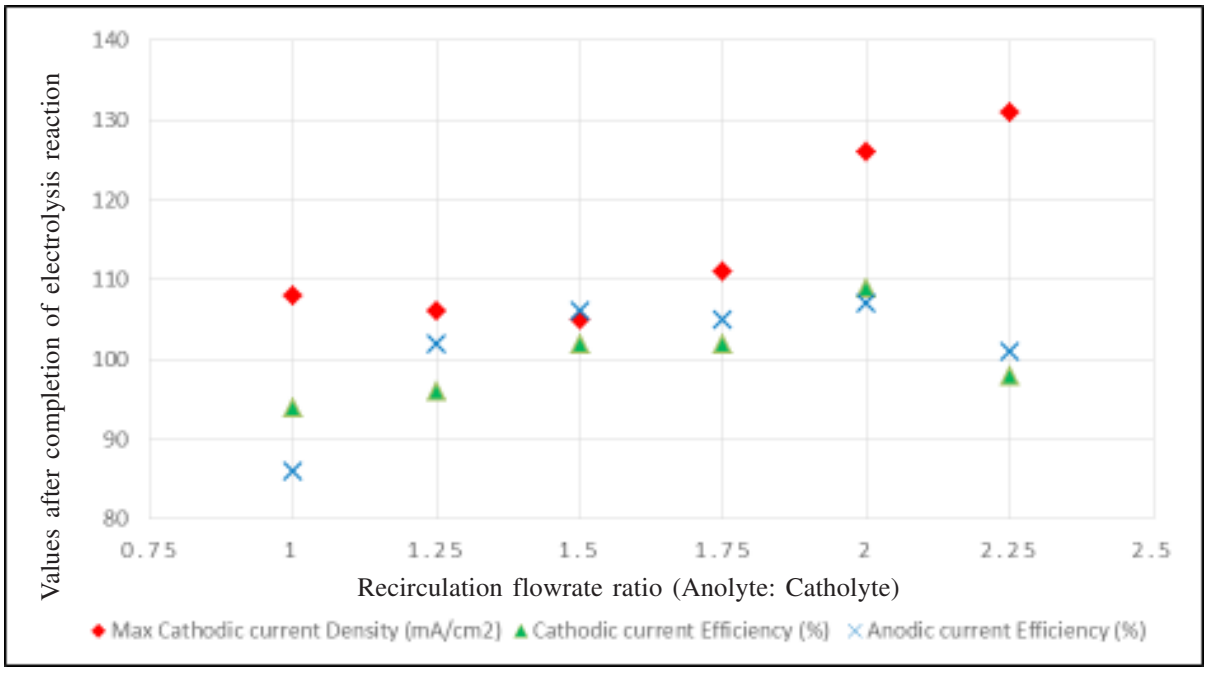


Fig 4: Effect of variation recirculation flowrate ratio of anolyte to catholyte

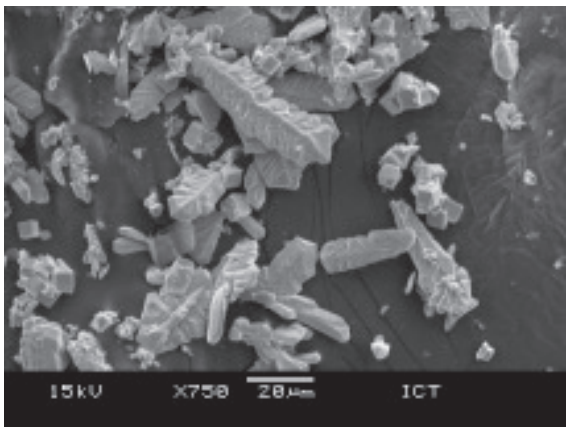
Table 1: Effect of increased concentration of electrolyte

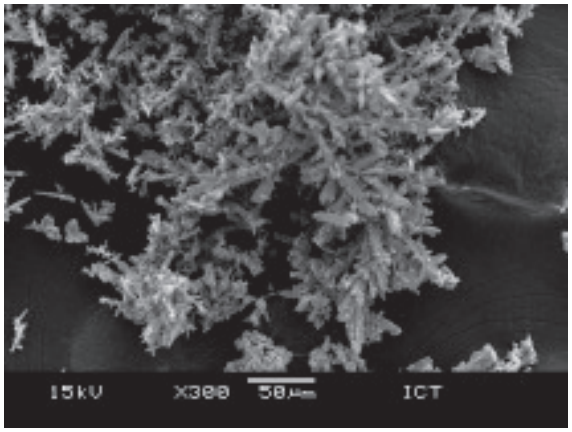
Sr.	HCl conc. (N)(with 0.5N CuCl)	Max Cathodic current density (mA/cm^2)	Cathodic current efficiency (%)	Anodic current efficiency (%)	Cu deposited (g/h)
1	3.5	177	113	107	39
2	4	195	132	115	40

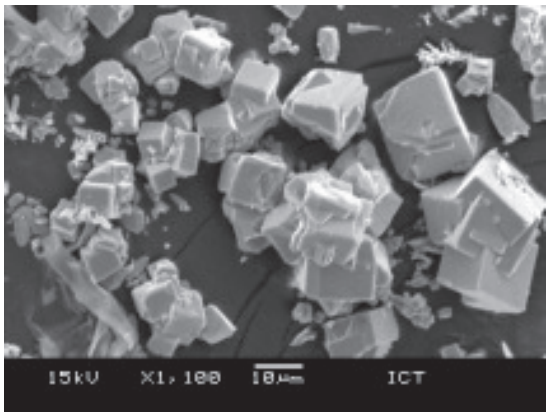
produced better results than 3.5N as summarized in table 1. The maximum cathodic current density increased to 195 mA/cm^2, copper deposition rate to 40g/h and the anodic current efficiency increased to 115%.

Characterization of copper powder

The SEM images of copper powder revealed a needle like dendritic growth (fig 5 (a) and (b)) and cubic structure as shown in fig 5 (d). The average particle size ranged in 40µ to 60µ.







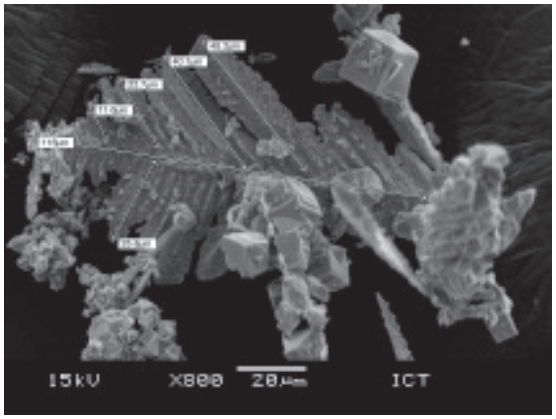


Fig 5: SEM images, Flowrate ratio; Anolyte: Catholyte= 1.75 (a) & (b), Flowrate ratio; Anolyte: Catholyte= 2.25 (c) & (d)

DISCUSSION

From experiments conducted, it was observed that the MMO performed better than platinum at higher voltages (above 0.9V). A detailed research is required to justify better performance of MMO than platinum at voltages above 0.9V. When flowrate ratio of anolyte to catholyte was increased, the current density and efficiencies

enhanced. This is probably due to increase in turbulence leading to effective mass transfer as there is increase in convective diffusion of ions at the electrode-electrolyte interface. This leads to decrease of diffusion layer thickness and consequently results in increase in current density and efficiency. Increase in electrolyte concentration increases the availability of ions in the solution thus enhancing the reaction. Dendritic growth of electrodeposited copper is attributed to the fact that chloride introduces anisotropy among various crystallographic directions and favors dendritic growth [16]. The concerned electrolysis system has chloride as an active electrolyte. Further research and more analysis are essential to understand the system in detail.

CONCLUSIONS

MMO coated on Ti mesh functioned significantly better as compared to pure platinum sheet in the CuCl electrolysis in HCl medium at voltage above 0.9V. Increasing the flowrate of anolyte as compared to catholyte increased the mass transfer and higher current density and efficiency were obtained. Increasing the electrolyte concentration enhanced the reaction and copper deposition rate significantly. SEM images confirmed the dendritic growth of copper and cubic structure. Current study reveals that MMO coated on Ti-mesh can be used as anode, an alternative to platinum. Also, recirculation flowrate plays an important role in electrolysis of CuCl. Further studies are required.

ACKNOWLEDGEMENTS

Venus Chaudhary acknowledges the contribution of SERB, Department of Science and Technology, Government of India, Confederation of Indian Industry and ONGC Energy Centre in facilitating research under Prime Minister Fellowship Scheme for Doctoral Research. G. D. Yadav acknowledges support from the R. T. Mody Distinguished Professor Endowment and the J. C. Bose National Fellowship of the Department of Science and Technology, Government of India. Financial assistance provided by Oil and Natural Gas Corporation Energy Centre, New Delhi, India is gratefully acknowledged. The authors are thankful to Director General and Head for their support and advice and Hydrogen Project Manager for cooperation.

REFERENCES

1. G. D. Yadav, P. S. Parhad, A. B. Nirukhe, D. Parvatlu, A. Bharadwaj, B. N. Prabhu, N. J. Thomas and D. M. Kale, patent US 8968697B2, “Hydrogen Production Method by Multi-Step Copper-Chlorine Thermochemical Cycle”, 2015

2. S. Suppiah, J. Li, R. Sadhankar, K. J. Kutchcoskie, M.A. Lewis, Study of Hybrid Cu-Cl cycle for nuclear hydrogen production, Nuclear Production of Hydrogen Third Information Exchange Meeting, Oarai, Japan, 5-7 October 2005.

3. M.A. Lewis, S. Niyogi, S. Ahmed, C. Fan, R. Sharna, M. Fedkin, M. Hickner, S. Lvov, D. Tatterson, L. Nitsche, L. Wedgewood, Membrane/Electrolyzer development in the Cu-Cl thermochemical cycle. Presented at the 2011 Hydrogen Program Annual Merit Review Meeting Arlington VA, May 12, 2011. http://www.hydrogen.energy.gov/pdfs/review11/pd013_lewis_2011_o.pdf

4. G.F. Naterer, S. Suppiah, L. Stolberg, M.A.Lewis, Z.L. Wang, I. Dincer, M.A. Rosen, K. Gabriel, E. Secnik, E.B. Easton, I. Pioro, S.N. Lvov, J. Jiang, J. Mostaghimi, B.M. Ikeda, G. Rizvi, L. Lu,A. Odukoya, P. Spekkens, M. Fowler, J. Avsec, Progress of international hydrogen production network for the thermochemical Cu-Cl cycle, Int. J. Hydrogen Energy 38 (2013) 740-759.

5. M. Serban, M.A. Lewis, J. Basco, Kinetic study of the hydrogen and oxygen production reaction in the copper-chloride thermochemical Cycle, Proceedings of the Argonne National Laboratory, 2003.

6. M. A. Lewis, S. Suppiah, J. Li, R. Sadhankar, K. J. Kutchcoskle, Study of hybrid Cu-Cl cycle for nuclear hydrogen production, Third Information Exchange Meeting, Oarai, Japan, 5-7 October 2005, 231-238. http://www.oecd-ilibrary.org/nuclear-energy/nuclear-production-of-hydrogen/study-of-

the-hybrid-cu-cl-cycle-for-nuclear-hydrogen-production_9789264026308-23-en

7. G.F. Naterer, S. Suppiah, L. Stolberg, M.A. Lewis, M. Ferrandon, Z. Wang, I. Dincer, K. Gabriel, M.A. Rosen, E. Secnik, E.B. Easton, L. Trevani, I. Pioro, P. Tremaine, S. Lvov, J. Jiang, G. Rizvi, B.M. Ikeda, L. Lu, M. Kaye, W.R. Smith,J. Mostaghimi, P. Spekkens, M. Fowler, J. Avsec, Clean hydrogen production with the Cu-Cl cycleprogress of international consortium, I: experimental unit operations, Int. J. Hydrogen Energy 36 (2011) 15472-15485.

8. A. Kettner, L. Stolberg, H. Li, A. Shkarupin and S. Suppiah, AECL's patent US9476132B2 "Electrolysis cell with multiple membranes for cucl/hcl electrolysis in hydrogen production", 2013.

9. K. S. Gabriel, Z. Wang and G. Naterer, patent US8628725B2, "Production of hydrogen from water using a thermochemical copper-chlorine cycle", 2008

10. M.A. Lewis, S. Ahmed, S. Lvov, C. Fan, II.E.2 Membrane/ Electrolyzer development in the Cu-Cl thermochemical cycle, FY 2012 annual report, DOE hydrogen and fuel cells program, 2012.

11. N. Sathaiyan, V. Nandakumar, G. Sozhan, J.G. Packiaraj, E.T. Devakumar, D. Parvatalu, A. Bhardwaj, B.N. Prabhu, Hydrogen generation through cuprous chloride-hydrochloric acid electrolysis, Int. J. Energy Power Engg. 4(1) (2015) 15-22.

12. S. Khurana, D.M. Hall, R.S. Schatz, M.V. Fedkin, S.N. Lvov, State-of-health of a CuCl electrolyzer during a 168-h test, Int. J. Hydrogen Energy 40 (2015) 62-69.

13. S. Ranganathan and E.B. Easton, Ceramic carbon electrode-based anodes for use in the Cu-Cl thermochemical cycle, Int. J. Hydrogen Energy 35(10) (2010) 4871-4876.

14. S. Ranganathan and E.B. Easton, High performance ceramic carbon electrode-based anodes for use in the cu-cl thermochemical cycle for hydrogen production, Int. J. Hydrogen Energy 35(3) (2010) 1001-1007.

15. G. D. Yadav, P. S. Parhad, A. B. Nirukhe, D. Parvatlu, A. Bharadwaj, B. N. Prabhu, N. J. Thomas and D. M. Kale, patent US 9447512B2, "Electrochemical Cell used in Production of Hydrogen using Cu-Cl Thermochemical Cycle", 2016

16. Barkey D., Oberholtzer F. and Q. Wu (1996), "Kinetic Anisotropy and Dendritic Growth in Electrochemical Deposition", Phys. Rev. Lett. 75, 2980