Comparison of novel anode materials for the production of hydrogen using CuCl/HCl electrolyzers

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Current H_2 gas supplies are primarily produced through steam methane reforming and other fossil fuel based processes [1]. This lack of a viable large scale and environmentally friendly H_2 gas production method has been a serious issue in the wide spread adoption of H_2 fuel cells. Two potential solutions to this problem are standard and hybrid thermochemical cycles. These cycles use waste heat to drive a series of thermochemical reactions resulting in the production of H_2 gas as well as the cycles starting materials. A promising example of this is the Cu-Cl hybrid thermochemical cycle. The cycle is composed of three steps:

- 1. CuCl₂ is heated to 400°C with H₂O to produce CuOCuCl₂ and HCl.
- 2. CuOCuCl₂ is heated to a further 500°C decomposing into O₂ and CuCl.
- 3. H₂ is evolved from HCl and CuCl is electrochemically oxidized to CuCl₂ in a PEM electrolyzer regenerating the starting material, releasing H₂ gas.

A major advantage of this cycle over others is that its heat requirements (400-500 °C) can be provided by relatively low grade waste heat. The cycle's heat requirements will also eventually be compatible with the temperature of Generation IV Supercritical Water Nuclear Reactors.[1] Additionally, the electrochemical step has a comparatively low voltage required to produce H_2 gas.

There are a number of areas of research involved in the CuCl-HCl hybrid thermochemical cycle. Of interest to our group is the electrochemical production of H_2 gas and in particular the production and characterisation of anode materials. We have previously shown that a platinum catalyst is not required at the anode as the oxidation is occurring at a transition metal centre. In addition to this we have produced and characterized high surface area ceramic carbon electrode (CCE) anode materials [2,3,4].

In aqueous media Cu(I) will form anionic complexes such as CuCl₂ or CuCl₃².[1] The slow transport of these species to the anode surface severely limits the overall electrochemical reaction. To facilitate the transport of these species we have produced CCE materials incorporating a selection of amine containing silanes with increasing numbers of primary and secondary amines. When protonated these amines allow for improved transport of anionic copper complexes. We have previously characterized the electrochemical behavior of these CCE materials in a half cell environment using cell polarization (Figure 1), cyclic voltammetry, and electrochemical impedance spectroscopy. In addition to this the CCE materials were characterized using thermogravametric analysis and transmission electron microscopy.

Here we will present the characterization of the previously produced CCE materials in a full cell

environment. Included in this we will examine the effects of varied silanes structure?, silane loading? (Figure 2), and total CCE mass loading on the overall cell performance and durability.

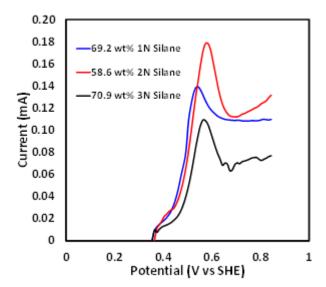


Figure 1: Linear sweep voltammograms obtained for novel anode electrodes produced from silanes containing 1,2, and 3 amine functional groups per silane molecule. Measurements were made in 0.2M HCl and 2mM CuCl under N_2 gas at 25 °C

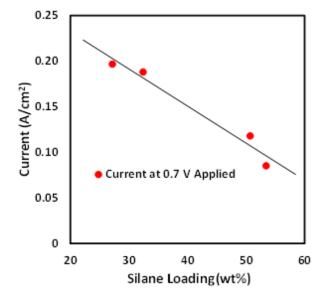


Figure 2: Relationship between CCE silane content and current response in a full electrolysis cell taken at 0.7 V vs. SHE.

References

- G.F. Naterer, et al., Int. J. Hydrogen Energy., 35, 10905-10926 (2010)
- 2. S. Ranganathan, P. S. R. Edge, E. B. Easton, ECS Trans., **41**, 111-120 (2012)
- 3. S. Ranganathan and E. B. Easton, Int. J. Hydrogen Energy, **35**, 4871 (2010).
- 4. S. Ranganathan and E. B. Easton, Int. J. Hydrogen Energy, **35**, 1001 (2010).