ABSTRACT

Global warming, climate change, and over-dependence on non-renewable fossil fuels demand long-term solutions to reduce CO_2 emissions and develop alternative and renewable fuels. The electrochemical CO_2 reduction reaction (CO_2RR) technique has been developed for the past few decades as a promising method to reduce the high CO_2 concentration in the atmosphere as well as to produce useful chemicals and fuels.

Numerous catalysts have been studied aiming at generating liquid products. However, it still has the limitation of low Faradaic efficiency (FE), selectivity, and stability. Therefore, producing liquid products (such as formate, methanol, and ethanol) by cost-effective catalysts may be more practical for the development of CO_2RR. Although many metals have been studied as catalysts for CO_2 electro-reduction, tin (Sn) can produce a considerable amount of formate. Formate formation, however, requires a high overpotential, which implies big energy losses. Furthermore, the selectivity of Sn towards a particular product is low and a mixture of products is obtained. Recently, bimetallic catalysts have been used for many electrochemical reactions with high activity and stability. To improve the catalytic process, % FE and product selectivity, Sn-based bimetallic nanocomposite catalysts for liquid product (especially formate) production through CO_2RR were prepared and evaluated in this thesis.

Most of this work focuses on the synthesis of Sn-based bimetallic electrocatalysts and electrochemical CO_2 reduction. The Sn-based bimetallic (Cu, Ag, Zn, Zr, Cd, etc.) nanoparticles were prepared by a simple, prosperous, and cost-effective chemical reduction method. Here we present the electrochemical conversion of CO_2 to liquid products in aqueous electrolyte media at 6.8 pH. The two-compartment cell (H type cell) was used for electrochemical measurements. The absorption maxima, the energy bandgap, surface morphology, catalytic composition, crystallinity, crystallite size, crystal facet, and electrochemical activity of the electrocatalyst were probed.

Initially, the general behavior of the electrode potential (CV, LSV) and CO_2 reduction activity over long periods of electrolysis were investigated, along with the effects of scans rate on current density and bulk electrolysis. The LSV was used to record the polarization curve/current response. Overall, the results obtained are consistent with those in the literature and cover important observations including the major reduction products on Sn-based bimetallic electrodes. We have similarly evaluated the faradic yields and rate constants for CO_2

reduction for the series of catalysts and have observed a higher faradic yield for formate production.

The electrochemical results show higher current density (~ -26 mA-cm^{-2} for Ag_2SnO_3 at -1.3 V *vs* Ag/AgCl and ~ -24 mA-cm^{-2} for $CuSn(OH)_6$ at -1 V *vs* Ag/AgCl), long term stability, product selectivity, and higher % FE on the bimetallic electrocatalyst. It was proposed that the current density during the electrolysis tends to become more negative in the case of Ag_2SnO_3 and $CuSn(OH)_6$, pointing toward an enhancement in the electrochemical activity of the electrode. However, the enhancement in electrochemical activity is found to be largely in favor of the CO_2 reduction (formate production) rather than HER.

The highest obtained % FE for the only liquid product (formate) was 89% at -1.3V with a Tafel slope of 174 mV-dec^{-1} and 82.8% at -0.9 V with Tafel slope value of 146 mV-dec^{-1} for Ag_2SnO_3 and $CuSn(OH)_6$ respectively. The % FE on bimetallic (Sn-Ag, Sn-Cu) electrocatalysts for the only liquid product (formate) were noticeably higher than the value cited in the literature for individual Ag, Cu, and Sn nanoparticles *i.e.*,39, 32 %, and 58 % respectively.

A very low overpotential (-0.66V) is obtained at the Sn-Cu bimetallic electrodes, with high current efficiencies generally comparable to that of the Sn and Cu controls and modified electrodes at similar current densities but at much higher overpotentials. This suggests a form of synergy at the active sites of the Sn-Cu interfaces which may have lowered the HER production, hence allowing similar amounts of formate to be produced at much lower overpotentials.

The catalysts surface was characterized by using SEM and shows the porous/sponge-like morphology. This allowed us to explore the effect of the surface morphology on the catalytic activity of bimetallic electrocatalysts. Our results suggested that the catalyst's sponge-like morphology or rough surface favors the CO_2 electrochemical reduction over the hydrogen evolution reaction (HER). Furthermore, on rough surfaces, the formation of formate is enhanced if no agglomeration has occurred.

In summary, we have reported the synthesis, characterization, and catalytic competency of 8 catalysts towards CO_2RR and utilized the preparative scale electrolysis to find out the current density, stability, % FE, size of nanoparticles, surface morphology, and product selectivity.