Electrocatalytic reduction of carbon dioxide on SnO$_2$/MWCNT in aqueous electrolyte solution

Shahid Bashir[a], Sk. S. Hossain[d], Sleem ur Rahman[e], Shakeel Ahmed[b], Amir Al-Ahmed[c], Mohammad M. Hossain[a],*

[a] Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
[b] Center for Refining and Petrochemicals, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
[c] Center of Research Excellence in Renewable Energy, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
[d] Department of Chemical Engineering, King Faisal University, Al-Hasa, Saudi Arabia
[e] Al Midad Holding, Al-Khobar, Saudi Arabia

ABSTRACT

This communication reports the activity of SnO$_2$/MWCNT (multi-walled carbon nanotubes) electrocatalysts for CO$_2$ reduction in an aqueous electrolyte solution using two compartment electrochemical cell. The effect of metal loading of the powdered catalysts (working electrode) on the reduction capabilities of CO$_2$ are studied, under ambient pressure and room temperature conditions. Electrochemical techniques such as linear sweep voltammetry and chronoamperometry are employed to get the current response (current density) for CO$_2$ reduction at different applied potentials. Current densities (C.D.) and the faradaic efficiencies (F.E.) of the products are the key performance indicators for any electrochemical process. The higher current densities and faradaic efficiencies for CO$_2$ reduction are obtained with the optimum SnO$_2$ content (20% by weight) on the high surface area MWCNT support. The 20% SnO$_2$/MWCNT catalyst shows remarkable activity for CO$_2$ conversion to formate with F.E. of c.a. 27.2% at a potential of −1.7V vs. SCE (Saturated Calomel Electrode). The higher activity is attributed to the uniform dispersion and more availability of active sites for CO$_2$ reduction.

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1. Introduction

Carbon dioxide is the major by-product of the petroleum, petrochemical and powerhouse industries. It is a greenhouse gas and contributes in the global warming phenomena. The alarming rate of accumulation of CO$_2$ in the atmosphere awakened the entire scientific community to take serious precautionary measures. Conversion of CO$_2$ to valuable products is the most viable way of utilizing CO$_2$. CO$_2$ can be converted into useful products in many different ways, but, for clean and sustainable energy future, renewable energy source is desired [1]. By electrochemical means, carbon dioxide can be easily transformed into useful products at room temperature and atmospheric pressure, provided that the cheap and carbon free source is available to generate electricity [2]. The pioneer work on CO$_2$ reduction was reported by Hori et al. in mid-1980's in which they carefully analyzed the product

distribution including liquid and gaseous phases in an aqueous electrolyte solution. However, the distribution of the reduction products and the selectivity strongly depend upon the type of the metal electrode used during cathodic CO$_2$ reduction process. In addition to the role of metal electrode, the electrolyte and reaction conditions (pH, temperature and pressure) play a vital role in the product distribution [3].

Most of the early work carried out in this research area, relied on the use bulk metal which acted as an electrode material in an aqueous electrolyte solution. Based on the findings of Hori et al. and other researchers [4–8] in the area of electrochemical carbon dioxide reduction, the electrodes are mainly classified into four groups depending on the product selectivity. These include, the formate formation metals (Hg, In, Pb, Sn), CO formation metals (Au, Ag, Zn), HER (hydrogen evolution reaction) metals (inactive for CO$_2$ reduction) and the only metal fall under the hydrocarbon formation category is Cu. With the advancement of fuel cell technology [9], the concept of porous electrocatalysts on high surface area conductive support is introduced. This new approach is beneficial in many aspects but the cost effectiveness and scalability of the process are the most significant ones. The

optimization of the active metal nanoparticles on the high surface area support enhances the number of adsorption and reaction sites, thereby by reducing the cost of unused metal content in the case of solid electrode. In this regard, many researchers around the globe including the present research group are dedicating their efforts in applying the concept of supported electrocatalysts for the carbon dioxide reduction process [10–12].

The proof of concept of carbon as a support material for the electrocatalytic reduction of CO_2 is well documented in the literature. The "support" material suitable for CO_2 electrocatalysis must be conductive enough to keep the flow of electrons from anode to cathode without Ohmic losses. Graphitic carbon, Vulcan carbon, carbon nanotubes and the graphene sheets are few examples which can be used for better charge transfer. However, the reactivity and product selectivity depend on the morphology, structure, pore size and BET surface area of the carbon material used. It was recently demonstrated, that the carbon nanotubes produce the nanoscale effect when the activity was tested for CO_2 reduction on the NiO/MWCNT catalyst. Carbon monoxide in addition to hydrogen was reported with different ratios suitable for the production of other valuable chemicals [10]. Hossain et al. (2014) reported the higher current activity of CO_2 to methanol on CNT (carbon nanotubes) based copper electrocatalyst with a faradaic efficiency of 38.5% due to the better dispersion of Cu nanoparticles and the availability of more reactive sites on the high surface area CNT support [11]. Tacconi et al. (2012) found methanol and isopropanol as major reduced products during electrocatalytic CO_2 reduction on the Pt/C-TiO2 nano composite matrices in the presence of pyridinium cation as a cocatalyst. The site proximity effect facilitated the multi electron transfer process for the conversion of CO_2 to alcohols due to high affinity of CO_2 adsorption on carbon [12]. Ampelli et al. (2014) studied the gas phase reduction of carbon dioxide to oxygenates using CNT and Pt/conjugated microporous polymer composite electrocatalyst. The high electrical conductivity of CNT promoted the mobility of electron while the high affinity of CO_2 adsorption on Pt/polymer active phase reduced the reactant to product specie [13].

In the present work, SnO2/MWCNT based electrocatalysts are investigated for CO_2 reduction in the presence of 0.5 M NaHCO3 aqueous electrolyte solution. Sn (Tin) cathode falls under the category of formate formation metals and exhibits high hydrogen over potentials during CO_2 reduction in the presence of water. Mahmood et al. (1987) first reported the higher partial current density of 35 mA/cm2 on a gas diffusion electrode comprised of Sn impregnated PTFE (Polytetrafluoroethylene) and Vulcan carbon black. CO in addition to formic acid was reported in an acidic pH under ambient pressure and temperature conditions [14]. Since then, there is an increasing trend in the research based on the Sn electrocatalyst on the carbon substrate. But more effort is needed to improve the overall activity of the process for formate production. Attempt is made in this regard to explore the activity of SnO2 electrocatalyst on the high surface area multi walled carbon nanotube support during current study. To best of our knowledge, the activity for CO_2 reduction on SnO2/MWCNT electrocatalyst was first studied (patented) by the present research group [15]. Since then, the electrocatalytic activity for CO_2 reduction have been reported on mixed phases of Sn/SnO$_x$ catalyst [16–18]. Recently, Sn/SnO$_x$ on MWCNT and Nitrogen doped MWCNT substrate have also been communicated for CO_2 reduction [19,20].

In this study, the activities of SnO2/MWCNT catalysts are presented for the electrochemical reduction of carbon dioxide. The electrocatalysts are prepared with different amount of metal oxide loading. The synthesized catalysts are characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Miscroscopy (TEM) and evaluated in a conventional half-cell reaction setup using sodium hydrogen carbonate as a supporting electrolyte solution. Linear Sweep Voltammetry (LSV) and Chronoamperometry (CA) are employed to measure the current densities and the liquid product analysis is done using Ion Chromatography (IC) to obtain the faradaic efficiencies.

2. Experimental

2.1. Catalyst synthesis and characterization

Electro catalysts used in this study were prepared by wet impregnation method with different weight loading of SnO2 on high surface area multi-walled carbon nanotubes (MWCNT). The carbon nanotubes were obtained from Cheap Tubes Inc. USA, while SnCl2 from Sigma Aldrich Co LLC Germany. MWCNT powder was functionalized by treating it with a mixture of HNO3 (30%) and H2SO4 (98%) at 100 °C overnight, followed by washing and drying at 120 °C to get the acid functionalized MWCNT powder. In a typical synthesis process, the calculated amount of tin chloride precursor was first dissolved in de-ionized water in the presence of tiny volume of HCl before adding it to acid functionalized MWCNT support. The resulting slurry was subjected to sonication for two hours. The samples were dried in an oven at 110 °C for 24 h followed by the calcination step which was carried out in a tubular furnace in an argon atmosphere for 3 h at 450 °C to decompose the chlorides from the tin precursor. Following the procedure as mentioned above, different SnO2/MWCNT catalyst samples were obtained with the loadings of 10–40 wt%.

The prepared electrocatalysts were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) techniques. BET surface areas of catalysts were measured using Quantachrome Autosorb analyzer by N2 adsorption. SEM images were taken by using a JEOL JSM-6460LV SEM microscope. The catalyst powders were grounded and then adhered onto the surface of the sample holder using double sided copper tape. The samples were coated with gold using ion sputter before taking the images. XRD patterns were acquired by using the Smart Lab (9 kW) Rigaku XRD diffractometer, with Cu-Kα radiation. An ultra-high resolution FETEM (JEOL, JEM-2100F), operated at an accelerating voltage of 200 kV was employed to capture the images of the metal dispersed on support surface. Diffraction data were collected between 10 and 80° 2θ and the JCPS powder diffraction database was used for XRD patterns identification. The crystal size of samples was measured by using well known Scherrer's equation.

$$d = \frac{K \times \lambda}{B \times \cos\theta} \tag{1}$$

where, B is the width of the XRD pattern line at half peak height (rad), λ is the wavelength of the X-ray (nm), θ is the angle between the incident and diffracted beams (°) and d is the crystal size of the powder sample (nm).

2.2. Electrochemical analysis

Electrochemical evaluation was carried out in a conventional two compartment half cell (H-cell) separated by ion exchange membrane. The detail of the electrochemical setup can be found elsewhere [10]. The working electrode (cathode) was prepared by sonicating 30 mg of catalyst powder in a volume ratio of (1:1:0.5) of Water:Isopropanol:Nafion solution (5% Nafion in isopropanol). The uniform slurry, thus obtained, was added layer by layer on a 2050-A carbon paper on 1 cm2 area. Carbon paper was kept on a hot plate at 80 °C while depositing the layer of electrocatalyst and finally dried in an oven at 120 °C for 12 h to remove the moisture