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Electrocatalytic reduction of CO₂ over dendritic-type Cu- and Fe-based electrodes prepared by electrodeposition

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Abstract

Here, we report on the enhanced electro-catalytic conversion of CO₂ to fuels using Cu and Fe nanofoams (NF) electro-deposited on different substrates which include Cu, Fe, Al, Ti, Fe-Cr-Ni alloy, Al grid/mesh, carbon-fibre based gas diffusion layer (GDL). Metal oxide based porous dendrite like structures were formed on these substrates with varying structural and catalytic properties. Also, we communicate the novel Fe nanofoam structures and preparation via electro-deposition techniques on GDL, Ti substrates. The nano-foam deposited on the metal substrates formed the working electrode and were tested for their catalytic performance on CO₂ reduction in the liquid phase cell prototype designed in the laboratory. The best net fuel productivity value attained was 313 $\mu\text{mol/hr.cm}^2$ per gram of catalyst. Also, we found that changing the substrate alters the foam structures and thereby, effecting the performance of the CO₂ reduction reaction. The CO₂ to fuels dependence on the substrate was also studied, to determine the true fuel productivity of the nanofoams. In-addition a time dependent fuel production study was also performed. To have a better comparison for different catalysts, all the reactions were performed at fixed conditions. But, for chosen nanofoam based catalytic electrodes, tests were performed at their respective reduction potentials observed from cyclic voltammetry and high faradaic efficiencies (F.E.) were achieved, ranging from - 42 % to 83 % for Cu NF with the best case F.E. for formic acid improved by 50% compared to literature and for Fe NFs, its 92 % to 95 % with high faradaic selectivity towards acetic acid.

Keywords: nanofoam (NF); electro-catalytic (EC); electro-deposition; dendrites; liquid phase cell.

Introduction

The combat against the rising world energy needs [1-4], the global climate change due to rising CO₂ and other green-house gases in the atmosphere, temperature rise, and other concerns [5-11] made the world research to race towards understanding and creating new paths to efficient and sustainable renewable energy technologies[3, 4, 6, 12]. One key path which addresses both these problems is artificial photosynthesis which utilizes renewable energy sources to convert CO₂ to fuels [13-19] using photo-electro catalytic (PEC) cells or artificial leafs [20-23]. This system is sub-divided into photo-catalytic [24, 25] and electro-catalytic [26-28] to ease the study and understanding of the fundamental aspects in these processes.

Nano-porous materials having high surface area, very low densities, large number of active sites are attractive materials for use in catalysis. Many studies towards CO₂ reduction with different metal/metal-oxide nanofoams (Zn, Sn, Bi, Pb, Ag, Au, Cu) already exist in literature [29-38] but, with Cu metal there are very few [36-38] and with Fe nanofoams are untouched yet. Studies on tuning the Cu nano-foams physical and structural properties, already reported in the past [39] and also, Fe

dendrites were synthesized via hydrothermal method and used for electro-magnetic applications [40-41].

In this work, we modelled Cu and Fe dendritic nanofoams based catalytic electrodes on various substrates of Cu, Fe, Ti, Al, FeCrNi, Al grid, GDL using electro-deposition techniques. We report, Fe dendrites and nanofoams, first-of-its-kind to be synthesized via electro-deposition and tested for CO₂ reduction to fuels. Also, we propose the deposition of the nanofoams on GDL, which would enable us to work in both liquid phase and well as gas phase conditions for CO₂ reduction to fuels. We provide a detailed comparison on the structural changes of nanofoams on different base metallic substrates and their respective CO₂ reduction activity. Moreover, we would like to communicate the high faradaic efficiencies (F.E. - 42 % to 92%) achieved and also, high F.E. selectivity (> 40 %) towards higher alkyl C₂-product (acetic acid) with low-cost, highly abundant Fe, nanofoam or dendrite based catalysts.

2 Experimental

2.1 Materials and Reagents

Chemicals used in our synthesis route are Iron (III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O], Iron (III) acetyl acetonate [Fe(C₂H₇O₂)₃ or Fe(acac)₃], Iron (II) sulphate heptahydrate [FeSO₄·7H₂O], Iron (III) sulphate hydrate [Fe₂(SO₄)₃·H₂O], Copper (II) sulphate pentahydrate [CuSO₄·5H₂O], Copper (II) acetate monohydrate [Cu(CH₃COO)₂·H₂O], hydrochloric acid (HCl, 37%), sulphuric acid (H₂SO₄, 95%), Sodium Hydroxide (NaOH), potassium bicarbonate (KHCO₃, 99.7%), Nafion perfluorinated resin were obtained from Sigma-Aldrich and used without any further purification. Gas Diffusion layer (GDL 25 BC) was obtained from Sigracet®. Nafion membrane (Nafion¹¹⁷) was obtained from Ion power and was pre-treated before use. Cu Foil, Al Foil, Titanium Foil were obtained from Sigma-Aldrich and were pre-treated before use. Fe Foil, Al grid were obtained from Good-Fellow and were also, pre-treated before use. Gas Diffusion Layer (GDL 25-BC) was obtained from Sigracet®.

2.2 Synthesis of the Nanofoams of Copper (Cu NF)

Nanofoams of Cu are synthesized using electro-deposition technique. Various kinds of nanofoams are achieved by altering conditions such as electrolyte, electrolytic P^H, electric current, time of deposition, substrate metal, and pre-treatment of the substrates. A schematic of this process is shown in the [Fig. 1](#).

Synthesis Method-I: (Cu and Fe Nanofoams)

Prior to the synthesis, the substrate metal foils (Cu foil, Fe foil, Ti Foil, Al foil, Al grid, Fe-Cr-Ni alloy) are mechanically polished using a P280 abrasive sheet and then, cleaned with distilled water and dried. Later, the foils are etched using dilute 0.5 M HCl aqueous solution for 5 minutes, and again, cleaned using distilled (DI) water and dried. This forms the cathode of the electro-deposition setup. The anode metal (Cu) foil also, undergoes above polishing and etching procedure. The anode and cathode are fixed at a separation distance of 1 cm. The electrolyte used is a mixture of 0.4 M CuSO₄ or Cu(CH₃COO)₂, 1.5 M H₂SO₄ and 50 mM HCl considered from the literature work [39]. The electro-chemical deposition of Cu NF is performed with a constant current of 1.2 A for time periods of 1 min, 2 min and 4 min. Also, in a specific case, with Fe as substrate, an under-potential deposition is performed for 30 min of deposition time. After the deposition, the NFs are cleaned using DI water carefully not to detach the NFs. The clean NF samples were dried at 80 °C overnight, and then,

calcined at 200 °C (5 °C rate) for 1 hr, thus forming the final dark brown-black working electrodes. On similar lines, Fe nanofoams were prepared on Fe, FeCrNi, Al substrates.

Synthesis Method-II: (Cu Nanofoams)

The pre-treatments of the substrate metal foils (Cu foil, Fe foil, Ti Foil, Al foil, Al grid, Fe-Cr-Ni alloy), the arrangement of the electro-deposition setup and final treatments are maintained as described in the *synthesis 1*. For GDL, it is directly used without any treatments. The only change made is the P^H of the electrolyte by addition of NaOH. The electrolyte used is 0.4 M $CuSO_4$, and added 1 M NaOH till the P^H reaches value of 12-13. The electro-deposition of Cu NF is performed with a constant current of 1.2 A for time periods of 0.5 min, 1 min, 2 min and 4 min. The smaller time depositions were performed to understand the initial formation stage flowery crystal growth of the foams as seen in SEM data.

Fig. 1 Schematic of Electro-deposition of Nanofoam on polished metal substrates.

Synthesis Method-II: (Fe Nanofoams)

The pre-treatments of the substrate metal foils (Fe foil, Ti Foil, Al foil, Fe-Cr-Ni alloy), the arrangement of the electro-deposition setup and the final treatments are maintained remain same as in the *synthesis 1*. Except for GDL, which is directly used and for Ti instead of HCl, HF was used for a better etching. The electrolyte used is 0.4 M $FeSO_4$ or $Fe_2(SO_4)_3$. We cannot add NaOH as it forms a strong Na salt on top of the substrate which blocks the foam formation. The electro-chemical deposition of Fe NF is performed with a constant current of 1.2 A for time periods of 15 sec, 30 sec,

45 sec, and 90 sec. As observed from the SEM data, the best times were - Fe(II) on Ti base (15 sec) ; Fe(II) on GDL or Fe base (90 sec) ; Fe(III) on GDL base (45 sec) ; Fe(III) on Ti or Fe or Al base (90 sec).

Liquid Phase Electrochemical (EC) Cell

The liquid phase cell prototype designed in the past in our laboratory [42] was used for performing the catalytic tests for different nanofoam based electrodes. The cell works on a three-electrode configuration, as it is graphically represented in Fig. 2. The cathode side houses the working electrode (circular, diameter 2.7 cm). A Pt ring makes up for the electric contact and closing of the external circuit between the working electrode and the counter electrode. A commercial Pt ball-edged rod (Amel) acts as the counter electrode, in the anodic compartment. And the reference electrode (Ag/AgCl) is placed close to the working electrode in the cathodic compartment of the cell. Constant voltage conditions are applied to the electrodes using a potentiostat-galvanostat (Amel mod. 2049A).

Fig. 2 Schematic of the experimental setup of liquid phase cell for CO₂ reduction to fuels.

The electro-catalytic cell is divided into two compartments: 1) anodic and 2) cathodic with the proton-exchange membrane (Nafion® 117) acting as the partition. A 0.5 M aqueous KHCO₃ electrolytic solution is used in the anodic compartment to generate H⁺ ions necessary for performing the reaction, while in the cathodic compartment a CO₂ (10 ml/min, pure) saturated electrolyte is flowed using an external tank and peristaltic pump. The fuels are analysed using Gas Chromatography-Mass Spectrometer (GC-MS) and Ion Chromatography (IC).

3 Results and Discussions

Characterization and Measurements

The nanofoams were characterized using techniques such as SEM, EDX, XRD, XPS and current profiles to determine the physical and structural properties. From the SEM surface and cross-sectional views, for the NFs via method-I, which formed leady dendrite-like structures with an actual weight of about 25-30 mg, measured by peeling of the NF from the metal base, and the respective average porosity of about 50 % (for average thickness of 15 μm).

For the NFs via method-II lead to the formation of truncated hollow-conical foamy structures with additional intra-porous structures. The NFs weight was measured to be about 10-15 mg by peeling and has an average porosity of 84 % with a Surface Area of about 38 cm^2 (per 1 cm^2 geometrical area).

SEM Morphological Measurements

Scanning Electron Microscopy (SEM) was performed by Phenom ProX Scanning Electron Microscope (SEM) equipped with EDX analyser to understand the structural and morphological surface characteristics of the nano-foams. *Fig. 3 (a) & (b)*, shows the surface with Cu foamy structures formed on Cu foil with deposition time = 1 min and 4 min, respectively (synthesis method-I). In the former figure, it can be observed that dendrite structures are yet to be formed, while in the later a flake-like structure formed bulk up into flakes due to increased time of deposition of the dendrites.

Fig. 3 SEM image (top view) of the Cu NF on Cu foil with deposition time (a) 1 min, (b) 4 min.

Fig. 3 SEM images of Cu NF on Cu (2 min) - dendrite structures (c) top view, (d) cross-section view.

Fig. 3 (c), shows the top view of the Cu dendrite structures formed on Cu foil with deposition time = 2 min. The dendrites resemble a leaf like model, with each leaf edge branching out into more leaves with smallest edge measuring about 100 nm. The leaf branches measure about 3, 5, 8 μm and the maximum about 13 μm before it collapses due to the increasing weight. The leaf branching approximately follows a Fibonacci sequence. Moreover, holey areas can be observed, which are formed due to the H₂ bubbles pushing out of the foamy structures formed during the electro-deposition. *Fig. 3 (d)*, shows the cross-sectional view of the NFs, evidencing a thickness of the Cu NF ranging between about 15-20 μm.

Fig. 4 SEM images of Cu NF on Fe foil (2 min) (a) top view, (b) dendrite close-up ; Cu NF on Al grid (2 min) (c) top view, (d) cross-section view.

Fig. 4 (a) & (b), shows the thick leaf-like Cu foams formed on Fe metal foil as the base substrate. It can be observed that these dendrites are more compact and closely packed as compared to that of the Cu foil based foams. Moreover, the lengths of these systems ranged from 100 nm to 100 μ m. Since the thickness and length are very high, they collapse under their own shear weight and form a dense intricate structure. *Fig. 4 (c) & (d)*, shows the Cu foam formed on an Al grid as base substrate. The foam is compact and thick. Not many dendrites are seen for Al as the base. In addition, from the cross-sectional view, we can calculate the thickness of the foam, which is about 4-5 μ m. Increasing the deposition time would make the foam peel-off since the base is cylindrical, thereby it has additional bending forces.

Fig. 5 SEM – method-II (a) Cu NF on GDL (2 min), (b) Cu NF on GDL cross-section, (c) Cu crystal flowers on GDL (30 sec), (d) Fe NF on GDL (45 sec), Fe NF on Ti - (e) Fe^{2+} (15 sec) & (f) Fe^{3+} (90 sec).

Surface Analysis

A quantitative surface analysis was performed by X-Ray photoelectron spectroscopy (XPS) using PHI 5000 VersaProbe II spectrometer with a monochromatic Al-K α X-ray source operated at 100 W, 20 kV.. The survey gives an insight into the oxidation state of the Cu foam formed. The C-1s binding energy of adventitious carbon (284.9) was used as the reference. *Fig. 6 (a)*, gives the general survey spectra of the Cu nano-foam, while *(b)* shows a high-resolution spectrum evidencing the peaks at 932.3 eV and 952.1 eV. They represent the characteristic binding energies for the CuO species, which are further confirmed by satellite peaks at 942.5 eV and 962.6 eV.

Fig. 6 (a) XPS wide scan survey of Cu NF on Cu (b) High-resolution spectra of the Cu 2p doublets.

Energy Dispersive X-ray spectroscopy (EDX)

EDX was carried out on different nano-foam samples, to get an idea of the composition of the different elements present. *Fig. 7* shows the EDX spectra for Cu NF on Cu foil, and the respective atomic concentrations are Cu (76.4 %), O (22.6 %), C (1%). Other samples EDX are discussed in the supplementary section.

Fig. 7 EDX spectra of the Cu nano-foam with base substrate as Cu foil.

Structural Analysis

X-Ray Diffraction (XRD) was performed to determine the crystal structure of the nano-foam using D2 Phaser Bruker diffractometer equipped with a Cu-K α radiation (1.5406 Å) source operating at 30 kV and 10 mA. A scan rate of 0.025°/s with a 2 θ range in 12° to 100°. **Fig. 8** shows the XRD patterns for Cu NF on Cu foil. From the diffraction pattern, the 3 peaks at 2 θ = 43.54°, 50.61°, and 74.25°, corresponding to the planes (111), (200) (220), respectively of the FCC of Cu metal. Also, 2 peaks are observed at 2 θ = 36.76° and 58.64°, which may correspond to CuO formed.

Fig. 8 XRD pattern of the Cu nano-foam with base substrate as Cu foil.

Current profile

The current profiles (in amperes) for the CO₂ reduction reactions, for the different Cu NFs on different base substrates and Cu Foil as a reference are shown below in **Fig. 9**. (i) A constant potential of -1.5 V is applied to the cell with the goal to compare these catalysts. It can be observed that the currents at the beginning of the reaction were quite high and then stabilize as an equilibrium P^H was achieved in the electrolytes in the anodic and cathodic compartments. Although the initial currents vary from 0.1 to 0.5 A, the equilibrium current lies in the range of 5 mA to 20 mA. (ii) Different potentials were applied, taken from cyclic voltammetry-reduction potentials to improve and achieve high faradaic efficiencies.

Fig. 9 Current profiles – (i) Constant Potential of -1.5V – (a) Cu NF on Cu, (b) Cu foil, (c) Cu NF on FeCrNi, (d) CuNF on (Al grid+Cu foil) ; (ii) Different potentials – (a) Cu NF on (Al grid+FeCrNi), (b) Cu NF on GDL, (c) Fe NF on GDL, (d) Fe NF on Ti (Fe^{2+}), (e) Fe NF on Ti (Fe^{3+}).

Cyclic Voltammetry (CV)

To understand the reduction potentials and achieve higher fuel efficiencies, CV was performed on individual catalytic electrodes from which the high Faradaic efficiencies (F.E.) shown in [Table 2](#) were accomplished. The CVs are shown in the [Fig. 10](#).

Fig. 10 CV curves - (a) CuNF on GDL, (b) FeNF on GDL, (c) FeNF on Ti (Fe^{2+}), (d) FeNF on Ti (Fe^{3+}).

Fuel Productivity

The fuels produced during the electro-chemical reduction of CO_2 were analysed using various techniques, which include IC, GC-Mass, and GC-TCD. The major liquid products detected in the liquid electrolyte on the cathode side were formic acid, methanol and acetic acid. Minor quantities of acetone, isopropanol and ethanol were also found. The gaseous products detected were H_2 , CH_4 and CO . The results are expressed in micromoles of the products obtained for a given time of the reaction

and the experiments were performed under same conditions, with potentiostatic (- 1.5 V), and constant CO₂ flow rate of 10 ml/min and the catalytic surface area ~ 5.7 cm², so that the catalytic activity of different materials can be well-compared under these fixed conditions as shown in [Table 1](#). Higher faradaic efficiencies were achieved with specific catalysts (chosen from the above fixed condition experimental results) with the catalytic reduction tests performed at different electric potential conditions acquired from the cyclic voltammetry curves as seen in [Table 2](#).

The fuel values for the NF electrodes synthesized via electro-chemical deposition using method-I and the respective plain metal electrodes (which acted as the base substrate for the foams) are shown in [Table 1](#). It is clearly evident that for the nano-foams the net C-products increased by several factors for different combinations of metal foams on metal substrates as compared to that of plain metal foil electrodes, thereby confirming that the activity is mainly due to the NFs. The plain metals showed near inert activity except for the Cu metal. In addition, there is a huge amount of H₂ production for the NFs (several orders higher than plain metals). The highest productivity obtained was for Cu NF on FeCrNi foil, which was about 44.6 μmol/hr C-products (i.e. 313 μmol/hr.cm² per gm of catalyst) and closely followed by a bi-electrode system (CuNF on Al grid + CuNF on Cu foil) with a value of 44.8 μmol/hr (240 μmol/hr.cm² per gm, since dual electrode). Here, the priority was not faradaic efficiencies, but to make a good comparison for various catalysts under constant conditions.

Also, for the NF based electrodes a better productivity of oxygenates and hydrocarbons with higher chain (C2-C3) was observed as compared to plain metal electrodes. Higher amounts of C-products along with higher H₂ values indicate that the NF electrodes utilize the energy supplied more efficiently. Moreover, there were gaseous products (CH₄, CO) observed for NFs, which were not seen for pure metal foil electrodes. The foams were synthesized via a simple technique and for some cases without application of electricity using only the reduction potential differences of metals, thereby enabling this method to be easily scalable for mass production of foams.

Table 1 Productivity for the CO₂ electro-catalytic reduction in liquid phase at fixed potential of -1.5 V for nano-foam electrodes (Synthesis type - I) (Units: μmoles per hr)

CATALYSTS (Synthesis type I)	FUELS (μmol·hr ⁻¹)									
	Formic Acid	Acetic Acid	Methanol	Acetone	Iso-Propanol	Ethanol	CH ₄	CO	H ₂	C-Products (NET)
Metal										
Cu Foil	12.48	0.06	0.37	0.01	0.01	0.02	2.07	2.80	264.52	17.81
FeCrNi Foil	0.12	0.00	-	-	-	-	-	-	22.83	0.12
Al Foil	0.58	0.00	-	-	-	-	-	-	89.28	0.58
Fe Foil	0.16	0.00	-	-	-	-	-	-	57.20	0.16
Nanofoam (NF)										
Cu NF on Cu (1 min)	1.96	0.07	0.00	0.00	0.00	0.00	-	-	97.82	2.03
Cu NF on Cu (2 min)	7.87	0.28	0.03	0.00	0.06	0.05	2.24	11.52	1069.55	22.05

Cu NF on Cu (4 min)	6.16	0.14	0.03	0.00	0.00	0.02	-	-	340.90	6.35
Cu NF on FeCrNi (2 min)	23.60	0.26	0.84	0.01	0.00	0.01	-	19.90	777.86	44.62
Cu NF on Al (2 min)	11.03	6.43	0.29	0.01	0.00	0.01	-	3.30	226.58	21.07
Cu NF on Fe*	0.16	0.42	0.37	0.00	0.00	0.00	2.25	2.13	61.58	5.33
Fe NF on FeCrNi. (2 min)	5.31	0.63	0.62	0.00	0.01	0.02	-	-	1538.04	6.59
Fe NF on Al (2 min)	0.36	0.82	0.07	0.00	0.00	0.00	-	-	480.27	1.25
Cu NF on (Al grid + Cu Foil)**	37.19	2.52	1.45	0.01	0.00	0.02	-	3.62	62.17	44.81

* Cu NF on Fe electrode prepared using under potential ; ** Combo-electrode Cu NF on (Al grid + Cu foil)

A time dependent study conducted on the products formed is shown in [Fig. 11 \(a\) & \(b\)](#), for two samples – Cu NF on FeCrNi foil and (Cu NF on Al grid + Cu NF on Cu foil). For these samples, the formation of H₂ and C-products continue to rise steadily with time. Also, reaction run-time was increased from 4 hr to 20 hr and also, the working electrodes were reused, to see, if there is a significant loss in the catalytic activity. The fuel productivity values were found to be steadily increasing with time and also, the re-use of the electrodes (2 times) showed a slight loss of about 5-10 % in products indicating the stability and long-term usage of the NF based electrodes.

Fig. 11 Time vs productivity of formic acid, acetic acid, CO and H₂ for (a) Cu NF on Inconel, (b) Cu NF on Al grid + Cu NF on Cu foil.

Table 2 Productivity for the CO₂ electro-chemical reduction in liquid phase cell for nano-foam electrodes (Synthesis type - II) in terms of Faradaic Efficiencies.

CATALYSTS (Synthesis type II) NanoFoams	Potential (V) <i>E</i> vs Ag/AgCl	Major C-Products	FUELS (Faradaic efficiency %), F.E.				
			Formic Acid	Acetic Acid	CO	H ₂	C-Products (NET)

<i>Cu NF on Cu</i>	- 1.50	HCOO ⁻ , CO, EtOH	37.24	1.67	7.30	48.02	49.0
<i>Cu NF on FeCrNi</i>	- 0.95	HCOO ⁻ , CO, CH ₃ COO ⁻	34.01	6.69	17.99	39.75	58.7
<i>Cu NF on GDL</i>	- 0.30	HCOO ⁻ , CO, CH ₃ COO ⁻	58.06	13.21	11.57	15.82	82.8
<i>Fe NF on GDL</i>	- 0.35	HCOO ⁻ , CH ₃ COO ⁻ , CO	44.57	27.16	20.27	7.63	92.0
<i>Fe NF on Ti (Fe²⁺)</i>	- 0.85	CH ₃ COO ⁻ , HCOO ⁻ , CO	24.48	48.81	18.69	7.11	91.9
<i>Fe NF on Ti (Fe³⁺)</i>	- 0.40	CH ₃ COO ⁻ , CO, HCOO ⁻	17.52	43.61	33.36	4.94	94.5
REFERENCES							
<i>Cu NF on Cu</i> [36]	-1.5	HCOO ⁻ , CO	37	-	7	55	47
<i>Cu Poly crystalline</i> [43]	-0.8 vs RHE	HCOO ⁻ , CO	26	-	18	50	48.5
<i>Cu Nanoparticles</i> [44]	-1.8	CH ₄ , C ₂ H ₄	3.5	-	0.1	49.7	35.7
<i>Cu NF hollow fibre</i> [37]	-0.5 vs RHE	CO, HCOO ⁻	10	-	72	14	85

Table 2 shows the NF electrodes synthesized via method-II and their respective fuel productivity in terms of faradaic efficiencies. High F.E.s were achieved by applying specific potentials chosen from cyclic voltammetry. For Cu NF on different base substrates (Cu, FeCrNi, GDL) the net-F.E. ranged from 42 % to 83 %, with highest F.E. for Cu NF on GDL. In-addition to having 75 % higher total F.E, it also has about 1.6 times higher formic acid efficiency (F.E., 58 %) compared to Cu NF cited in literature [36] and much higher when compared with state-of-the-art Cu crystalline electrodes. A comparison of the results is provided in the *Table 2* for convenience.

For the Fe NFs, the achieved F.E. was about 92-95 % with the best F.E. for *Fe NF on Ti (Fe³⁺ precursor)*. Moreover, it can be noticed that there is significant improvement and shift towards the higher alkyl product (acetic acid) with highest value of 49 %. Although, *Fe NF on GDL (F.E. 92 %)* is only slightly lower, it has an added advantage to the electrode which can be used in gas phase catalytic systems (electrolyte-less cells), in-addition to conventional liquid phase cells.

Conclusion

Here, we presented two main types of catalysts and their respective electro-catalytic CO₂ reduction study. The first type is Cu based nanofoams or dendrite-like structures, which are formed via electro-deposition on different substrates (Cu, Fe, FeCrNi, Al, Al grid, GDL) and tested for CO₂ reduction. With this, we showed that the NFs structure and catalytic activity are both altered greatly with varying base substrates, (the best productivity of 313 $\mu\text{mol/hr.cm}^2$ per gm of catalyst *Cu NF on FeCrNi*). We tried to improve the electro-deposition conditions used to synthesize the Cu NF, thereby created new set of Cu NF electrodes with much uniform and higher porous foams, which in-turn proved to be better catalysts for CO₂ reduction, with the a substantial improvements in productivity, with the highest faradaic efficiency (83 %) seen for Cu NF on GDL at -0.3V/Ag/AgCl. This is also, nearly twice the efficiency than the best Cu NFs cited in literature [36] working in simple, non-ionic electrolytes.

CO₂ reduction test were performed using just the base substrates alone to see their contribution to the NF performance, and found that the activity is mostly dependent on the NF alone.

Also, time dependant study was performed to see the loss in catalytic activity as the reaction progresses.

The second work, was successful development of precise conditions of electro-deposition of uniform, highly porous Fe nanofoams and dendritic structures. The novel Fe NFs, modelled are first-of-its-kind, to be prepared via a cost effective and simple electro-deposition technique. Also, the use of Fe NFs in CO₂ electro-catalytic reduction is the first ever to be reported. This opened doors towards the highly efficient, very cheap, abundant Fe NF based catalytic electrodes in CO₂ reduction to fuels with faradaic efficiencies ranging from 92-95% for Fe NFs on GDL, and Ti substrates. In-addition, Fe NF showed to be more effective towards reducing CO₂ to higher alkyl products (best Faradaic efficiency for acetic acid, 49%). Another, important outcome was to be able to develop nanofoam on GDLs, which put-forward possible usage of the NF based catalysts in both electrolyte-less (gas phase) and liquid phase conditions moving us a step closer towards artificial leaves.

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