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# Effect of Supporting Salts on Photoelectrochemical Reduction of CO<sub>2</sub> in Methanol with Cu Cathode and TiO<sub>2</sub> Photoanode

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**Abstract**— In the present study, we demonstrate that the activity and selectivity of products from the CO<sub>2</sub> photo electrochemical reduction with TiO<sub>2</sub> photo anode and Cu cathode can be tuned by simply changing alkali metal cations and halide anions in the electrolytes. The development of methods to convert CO<sub>2</sub> into value fuel with high-energy content has received much attention. Comparing the current density and Faradaic selectivity of the reduction products from CO<sub>2</sub> in the presence of various cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>) and anions (Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>), the selectivity of reduction products depends on the nature of the added cations and anions. As the cation size effect, the cathode activity improved, the Faradaic efficiencies for H<sub>2</sub> and CH<sub>4</sub> decreased and the Faradaic efficiencies for CO, C<sub>2</sub>H<sub>4</sub>, and HCOOCH<sub>3</sub> increased. Also, in the presence of adsorbed I<sup>-</sup>, the induced negative charge of electrode has a remarkably positive effect favoring the formation of CH<sub>4</sub>. These results presented an easy way to enhance the CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> production during the CO<sub>2</sub> photo electrochemical reduction with TiO<sub>2</sub> photo anode and Cu electrode.

**Keywords** — Photo electrochemical reduction of CO<sub>2</sub>, TiO<sub>2</sub> photo anode, Methanol, Cu cathode

## I. INTRODUCTION

An appealing option for the conversion of solar energy to valuable feedstocks for our chemical industries and fuels is the photo electrochemical reduction of CO<sub>2</sub> using semiconductor materials [1]. Among the CO<sub>2</sub> reduction products, hydrocarbons such as ethylene (C<sub>2</sub>H<sub>4</sub>) and methane (CH<sub>4</sub>) have high energy densities and commercial value [2]. The type of products formed during CO<sub>2</sub> electrochemical reduction is significantly impacted by the electrolytes used, electrolyte pH, potentials applied, and the morphology and surface geometry of the copper surfaces [2]. Methanol is better solvent of CO<sub>2</sub> than water [3]. In this study, the photo electrochemical reduction of CO<sub>2</sub> with Cu cathode and TiO<sub>2</sub> photo anode was investigated in methanol-based electrolyte using various supporting electrolyte salts.

## II. METHODS

### A. Electrode Preparation

The titanium foil (30 × 20 mm, 0.2 mm thickness, 99.5 %) was purchased from Nilaco Corp. Ti foil was first degreased by sonication in acetone, ethanol and pure water and then dried in air. TiO<sub>2</sub> nanotube (TNT) photo anode was synthesized via a commonly used electrochemical anodizing method [4]. For typical synthesis, a two electrode system was assembled by using Ti foil and Pt foil as working electrode (WE) and counter electrode (CE), respectively. The electrolyte, 1 vol% hydrogen fluoride solution containing 10 % methanol, was used. The anodization was carried out at 20 V for 30 min under ultrasound condition. Finally, the fabricated electrode was thoroughly washed by pure water and then calcined at 700 °C for 2 hours at a heating rate of 10 °C/min in order to improve the crystallinity.

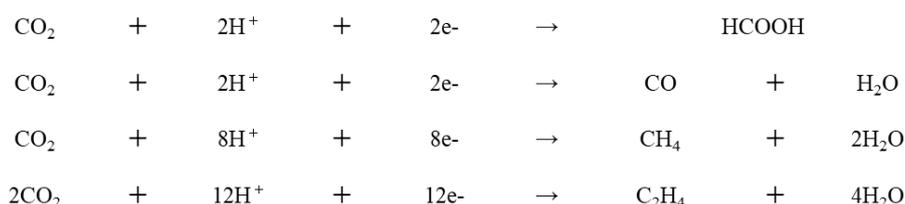
The copper foil (30 × 20 mm, 0.1 mm thickness, 99.96%) was purchased from Nilaco Corp. First, Cu foil was polished mechanically using an alumina polishing suspension down to 1.0 μm, then rinsed with pure water, and dried under air. Next, Cu foil was electro polished in concentrated phosphoric acid by a DC constant voltage/current power at a potential of 3.0 V for 140 s with a Pt foil counter electrode, followed by rising with pure water and drying with a stream of air.

### B. Photo electrochemical cell and experimental conditions

The experimental conditions for the photo electrochemical reduction of CO<sub>2</sub> in the methanol are shown in Table 1. A standard three-electrode H-type electrochemical cell was used. The cathodic and anodic compartments were

separated by an Aldrich Nafion 117–type ion–exchange membrane (0.18 mm thickness). TiO<sub>2</sub> electrode, Cu electrode, and Ag Q.R.E. served as working, counter, and reference electrodes, respectively. The supporting salts such as XCl (X = Li, Na, Cl, Rb, and Cs) and NaY (Y = Cl, Br, and I) (Nacalai Tesque, Inc.) in methanol were used as the catholyte. The 1.2 M NaHCO<sub>3</sub> (Nacalai Tesque, Inc.) solution was used as anolyte. A potentiostat (HA-3001A) was used for controlling and measuring the potentials/currents under ambient pressure and temperature. Prior to CO<sub>2</sub> reduction, the catholyte was saturated with CO<sub>2</sub> gas (99.999%, Kawase Industry) for 2 hours at a flow rate of 60 mL/min. After CO<sub>2</sub> gas bubbling into catholyte, the working electrode (TiO<sub>2</sub> photo electrode) was irradiated by a UV light (365 nm) for the photoelectrochemical reduction of CO<sub>2</sub> in the methanol.

The Faradaic efficiencies of formation for the main products were calculated from the total charge passed during photo electrolysis. The main products can be formed on the surface of Cu electrode via the following reactions.



The gaseous products obtained during electro reduction were collected in a gas collector and were analyzed by gas chromatography. Products soluble in the catholyte were analyzed by high performance liquid chromatography (HPLC).

Table 1: Experimental conditions

Cell	H-type grass cell	carbon dioxide	99.9999%
potentiostat/galvanostate	Hokuto HA-3001A	Anode potential (V)	+1.0 V vs Ag.Q.R.E.
Electrode		Temperature	room temperature
Working electrode	TiO <sub>2</sub> foil (30 × 20 mm, 0.2 mm thickness)	Total charge passed	50 C
Counter electrode	Cu foil (30 × 20 mm, 0.1 mm thickness, 99.96%)	Light source	UV LED (365 nm)
Reference electrode	Ag Q.R.E.	Product analysis	
Catholyte	0.1 M LiCl, NaCl RbCl, CsCl, NaBr, NaI in CH <sub>3</sub> OH	Gaseous products	gas chromatography FID (GL Sciences GC-353B, GC-4000 Plus) TCD (GL Sciences GC-320, GC-3200)
	0.07 M KCl in CH <sub>3</sub> OH	Liquid products	HPLC with UV-Vis detector (LC-10AT, SPD-10AV)
Anolyte	1.2 M NaHCO <sub>3</sub> in water		

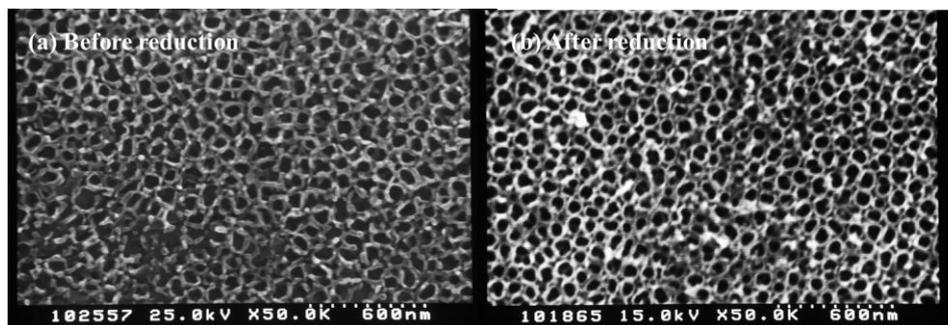


Fig. 1: SEM images of TiO<sub>2</sub> photo anode calcined at 700 °C for 2 hours (a) before and (b) after reduction

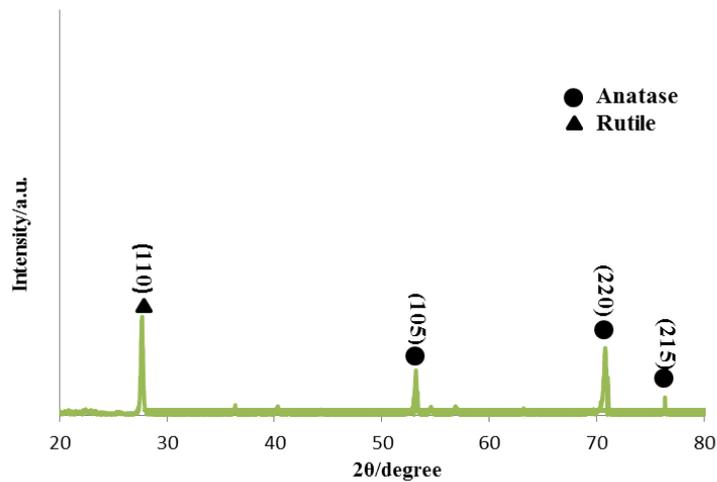


Fig. 2: XRD patterns of TiO<sub>2</sub> nanotube calcined at 700 °C for 2 hours

### III. RESULTS AND CONCLUSION

#### A. Characterization of TiO<sub>2</sub> electrode

Figure 2 demonstrates the typical SEM images of TiO<sub>2</sub> electrode arrays before and after photo electrochemical reduction of CO<sub>2</sub>. It can be seen from the top view image of the free-standing TiO<sub>2</sub> nanotube (TNT) arrays that the tubes have ordered arrangement with an average diameter of ~90 nm [3] [6]. From Figures 2 (a) and (b), there were no changes of nanotube structures before and after CO<sub>2</sub> reduction.

The XRD patterns of TNT are shown in Figure 3. The XRD of TNT exhibited several diffraction peaks at 53.2 °, 70.8 °, and 76.2 °, indexed to the (105), (220), and (215) crystal planes of anatase phase TiO<sub>2</sub>, respectively, and several diffraction peaks at 27.7 °, indexed to the (110) crystal planes of rutile TiO<sub>2</sub> [4] [5]. The XRD pattern of TNT showed the diffraction peaks of both anatase TiO<sub>2</sub> and rutile TiO<sub>2</sub>, which further proves that TNT calcined at 700 °C for 2 hours is anatase/rutile mixed phase structure (A/R-TiO<sub>2</sub>). The high activity of A/R-TiO<sub>2</sub> is due to lower recombination and more efficient separation of photo-generated electron-hole pairs in A/R-TiO<sub>2</sub> [8].

#### B. Cation effects on Cu electrode

In order to examine the electrochemical behavior with the various alkali metal cations, the photo electrochemical reduction of CO<sub>2</sub> with TiO<sub>2</sub> photo electrode and Cu cathode in CO<sub>2</sub>-saturated LiCl (0.1 M), NaCl (0.1 M), KCl (0.07 M), RbCl (0.1 M), and CsCl (0.1 M) in methanol based catholyte was observed at an applied potential of 1.0 V vs. Ag A.Q.E. for the anode. The methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), carbon monoxide (CO), and methyl formate (HCOOCH<sub>3</sub>) were the principal products identified by the analytical system used in this study. Oxygen was detected from the anodic compartment. The influence of cation size on the Faradaic efficiencies (FEs) and the C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> ratio for CO<sub>2</sub> reduction products produced on Cu cathode at 1.0 V vs Ag Q.R.E. are given in Figure 3 (a) and (b), respectively. The total Faradaic efficiency for CO<sub>2</sub> reduction products increased by ~27.0 %, as the cation size increases from Li<sup>+</sup> to Cs<sup>+</sup>. Figure 3 (a) shows that the FEs for H<sub>2</sub> and CH<sub>4</sub> formation decreased and the FEs for C<sub>2</sub>H<sub>4</sub> formation increased with increasing cation size. Figure 3 (b) also shows that the ratio of FEs of C<sub>2</sub>H<sub>4</sub> to CH<sub>4</sub> formed on Cu cathode increased from 1.14 for Li<sup>+</sup> to 159 for Cs<sup>+</sup>. Figure 4 (a) shows that the current density tended to increase with increasing cation size at a fixed potential. However, there was little effect of cations on current density. Figure 4 (b) shows the effect of bulk pH before and after reduction. The bulk pH increased during photo electrochemical reduction of CO<sub>2</sub> from ~5 to ~8. We could estimate that near-neutral pH is optimal. Since the distribution of dissolved CO<sub>2</sub> between molecular CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> is strongly dependent on pH, a high pH leads to a reduction in the concentration of molecular CO<sub>2</sub> due to its rapid consumption by hydroxyl anions to form HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, which occurs at much higher rates than the rate of CO<sub>2</sub> reduction. This is detrimental to CO<sub>2</sub> reduction, since only molecular CO<sub>2</sub> undergoes reduction [9].

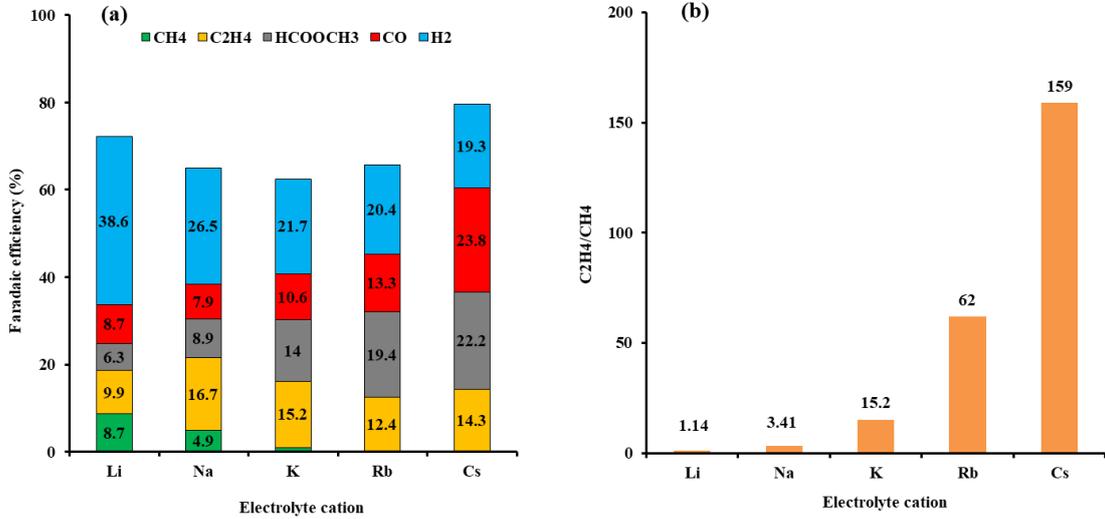


Fig. 3: Influence of cation on (a) Faradaic efficiency (FE) and (b) the ratio of FEs for C<sub>2</sub>H<sub>4</sub> to CH<sub>4</sub> by CO<sub>2</sub> photoelectrochemical reduction at 1.0 V vs Ag Q.R.E. in methanol based catholyte with the supporting salts such as XCl (X = Li, Na, Cl, Rb, and Cs)

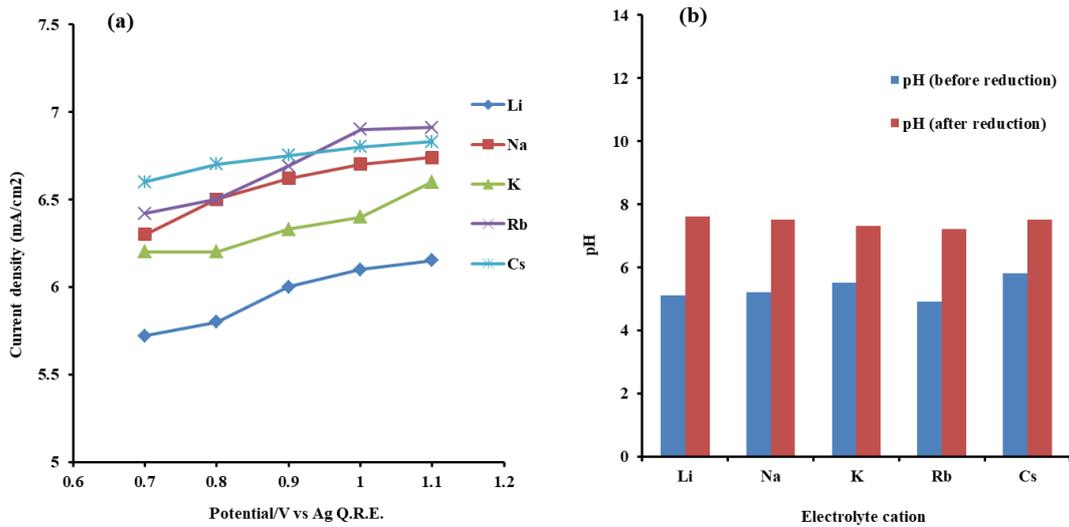


Fig. 4: Influence of cation on (a) current density and (b) electrolyte pH by CO<sub>2</sub> photo electrochemical reduction at 1.0 V vs Ag Q.R.E. in methanol based catholyte with the supporting salts such as XCl (X = Li, Na, Cl, Rb, and Cs)

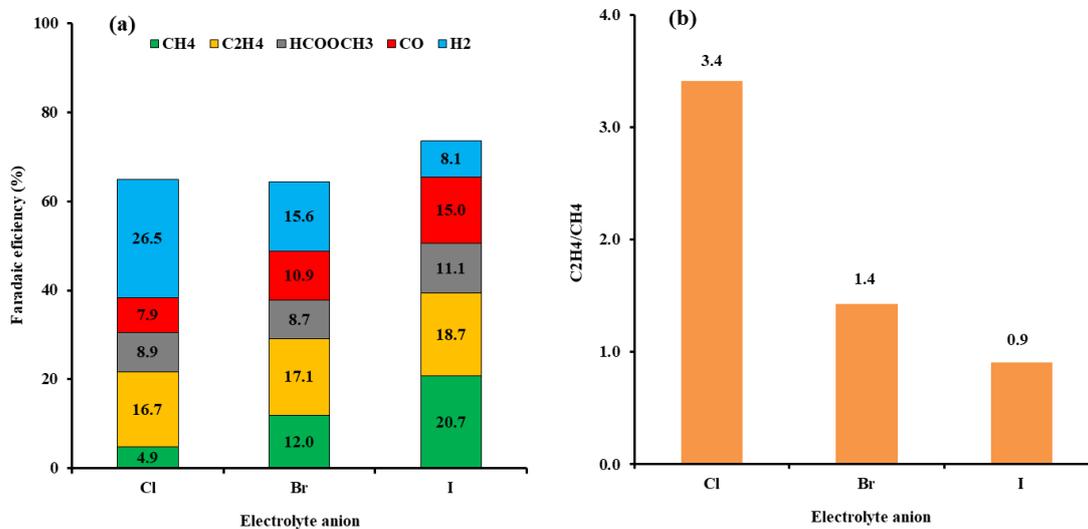


Fig. 5: Influence of anion on (a) Faradaic efficiency (FE) and (b) the ratio of FEs for C<sub>2</sub>H<sub>4</sub> to CH<sub>4</sub> by CO<sub>2</sub> photo electrochemical reduction at 1.0 V vs Ag Q.R.E. in methanol based catholyte with the supporting salts such as NaY (Y = Cl, Br, and I)

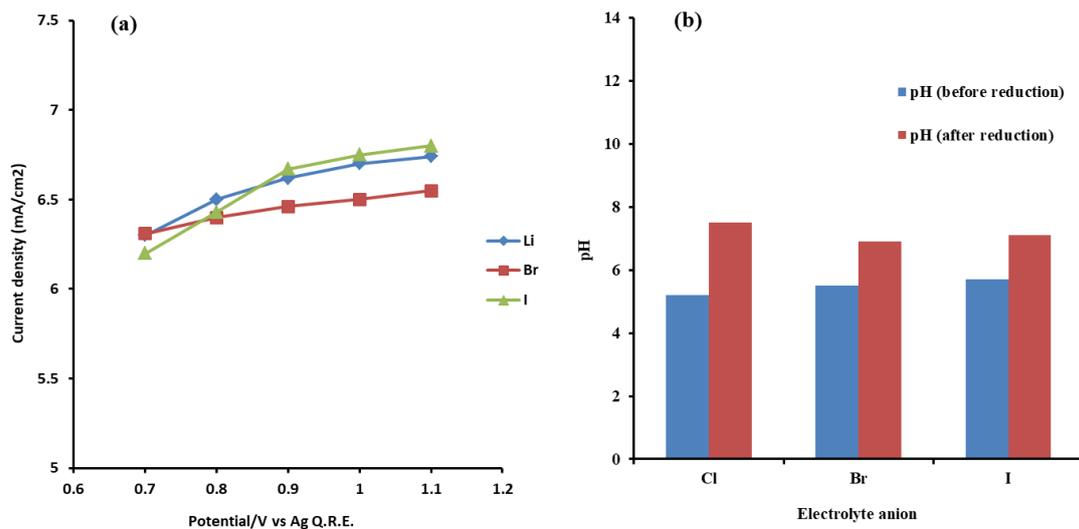


Fig. 6: Influence of anion on (a) current density and (b) electrolyte pH by CO<sub>2</sub> photo electrochemical reduction at 1.0 V vs Ag Q.R.E. in methanol based catholyte with the supporting salts such as NaY (Y = Cl, Br, and I)

### C. Anion effects on Cu electrode

The effect of anions on the catalytic activity of Cu was studied by performing the photo electrochemical reduction of CO<sub>2</sub> in the presence of different halides of 0.1 M NaCl, NaBr, and NaI. The influence of anion on the Faradaic efficiencies (FEs) and C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> ratio for CO<sub>2</sub> reduction products produced on Cu cathodes at 1.0 V vs Ag Q.R.E. are given in Figure 5 (a) and (b), respectively. We observed that the FEs of reduction products were affected by the nature of the halide and followed the trend: Br<sup>-</sup> < Cl<sup>-</sup> < I<sup>-</sup>. In particular, iodide appeared to have a negative effect on the H<sub>2</sub> formation, and a positive one on the CH<sub>4</sub> formation. CH<sub>4</sub> formation was highest in the presence of I<sup>-</sup>, reaching a FE toward CH<sub>4</sub> of ~20 %, leading to a lower FE ratio of C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub>. By contrast, H<sub>2</sub> formation was suppressed to the FE of 8.1 % in the presence of I<sup>-</sup> in comparison to Cl<sup>-</sup> and Br<sup>-</sup>. Therefore, I<sup>-</sup> induced more selective CO<sub>2</sub> reduction to CH<sub>4</sub> formation. Figure 6 (a) shows that there was little effect of halides on current density. Figure 6 (b) shows the effect of bulk pH before and after reduction. This pH value effect followed the same trend with the effect of cation.

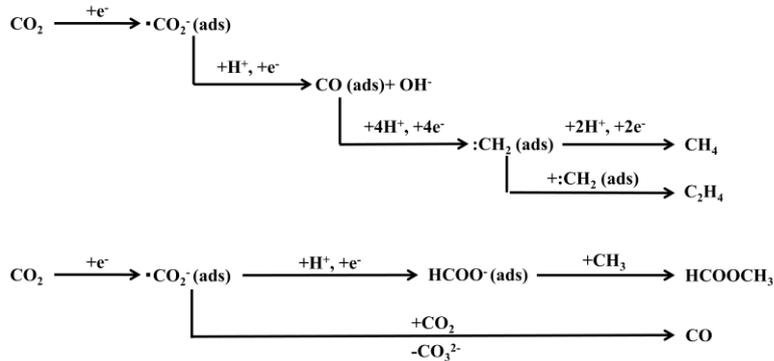


Fig. 7: Reaction pathway for the photo electrochemical reduction of CO<sub>2</sub> in methanol

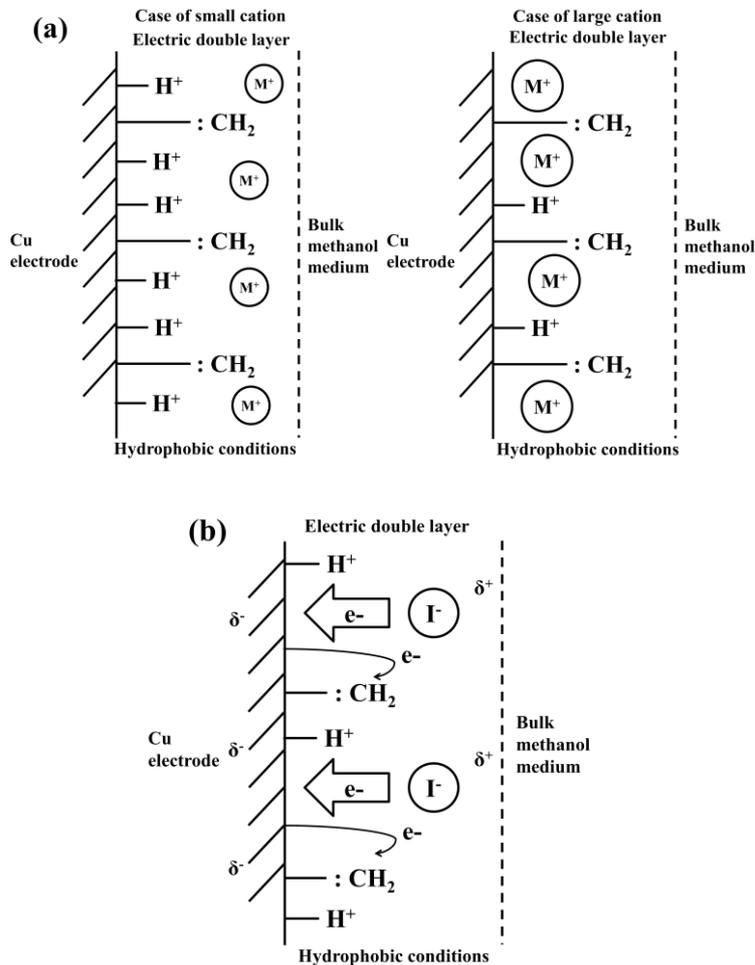


Fig. 8: The schematic cross-sections on the (a) cationic and (b) anionic chemical species onto the copper electrode

#### D. Reaction Mechanism

When TiO<sub>2</sub> photo anode is irradiated with UV light, the electrons of valence band (VB) are excited to conduction band (CB) with the same amount of holes simultaneously generated in the VB, and then the photo-generated electrons are injected from the TiO<sub>2</sub> photo anode to the cathode. The photo-generated electrons react with CO<sub>2</sub> which is adsorbed on cathode, and then CO<sub>2</sub> radical anion is formed [4].

The photo electrochemical reduction of CO<sub>2</sub> is, apparently, a very complex process. Figure 7 suggests that the



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reaction pathway of methane, ethylene, carbon monoxide, and methyl formate formation for the photo electrochemical reduction of  $\text{CO}_2$  in methanol [2][3][13]–[15]. Hydrocarbons are yielded by a series of simultaneous or consecutive electronation/protonation steps. The adsorbed  $\text{CO}_2$  radical anion formed in the first electronation step undergoes a second electronation/protonation to yield adsorbed CO as the key intermediate. From a succession of four electronation/protonation steps, an adsorbed reactive methylene group forms, and this may either stabilize as a methane molecule by a subsequent double electronation/protonation sequence or dimerize to form ethylene. For the formation of methyl formate and CO, we assume the usual pathway, which involves a one-electron reduction followed by a second electronation/protonation and the reaction of methanol to yield methyl formate, and by the disproportionation of  $\text{CO}_2$  radical anions to neutral CO molecules and dinegative carbonate ions.

It could be considered that the effects of alkali metal cations and halide anions on the catalytic activity and selectivity were attributed to the cationic and anionic chemical species on the copper electrode [8]–[12]. The schematic cross-sections on the cationic and anionic chemical species onto the copper electrode are shown in Figure 8 (a) and (b), respectively. From Figure 8 (a), small cations such as  $\text{Li}^+$  were not susceptible to being adsorbed at the electrode surface as compared to large ones, because they have a larger hydration power. In addition, small cations supply protons for the photo electrochemical reduction. The conversion of adsorbed reactive methylene group to methane requires the presence of adsorbed hydrogen. Therefore,  $\text{CH}_4$  formation is favored with small cations. Conversely, large cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  were relatively adsorbed at the electrode surface. Therefore, the  $\text{C}_2\text{H}_4$  formation is favored with large cations because dimerization efficiency of methylene intermediate increases. The effect of halides on the  $\text{CO}_2$  reduction can be explained with the donation or retention negative charge of the adsorbed halides in Figure 8 (b). The retention of the negative ionic charge in the chemisorbed state increases in the order:  $\text{I}^- < \text{Br}^- < \text{Cl}^-$ . In other words, this means that  $\text{I}^-$  more easily donates its more negative charge to the Cu surface. Hence, this might enhance the electronation/protonation of methylene intermediate for the  $\text{CH}_4$  formation.

#### IV. CONCLUSION

The photo electrochemical reduction of  $\text{CO}_2$  with Cu cathode and  $\text{TiO}_2$  photo anode in methanol was investigated for various supporting salts. The physical characterization of  $\text{TiO}_2$  photoelectrode shows the  $\text{TiO}_2$  obtained nanotubes structure and anatase/rutile mixed phase structure. The reduction products were confirmed the formation of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , CO and  $\text{HCOOCH}_3$ . The selectivity of the photo electrochemical reduction products of  $\text{CO}_2$  on Cu cathode in methanol depended remarkably both cationic and anionic species. The monitoring for the effect of cation on selectivity of reduction product with Cu cathode indicated that the main product of hydrocarbon by photo electrochemical reduction of  $\text{CO}_2$  with small size cation such as  $\text{Li}^+$  was  $\text{CH}_4$ , whereas the main product with large size cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  was  $\text{C}_2\text{H}_4$ . Also, the photo electrochemical reduction of  $\text{CO}_2$  in methanol based electrolyte with iodide anion showed the favorable higher catalytic selectivity toward  $\text{CH}_4$ .

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