

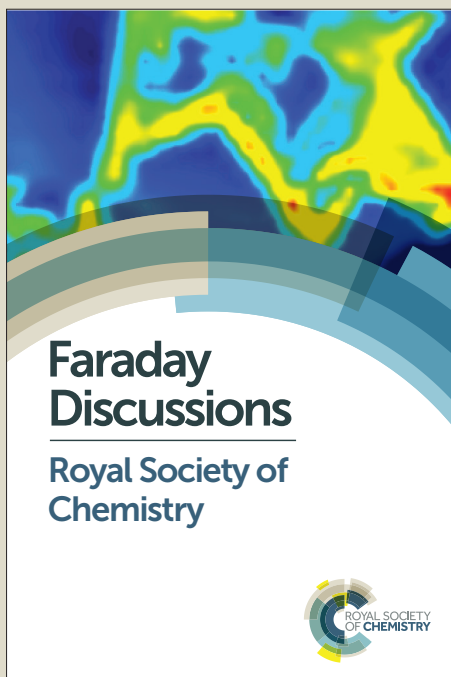
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Electrochemical CO₂ Reduction with Low Overpotential by Poly(4-vinylpyridine) Electrode for Applying on Artificial Photosynthesis

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Pyridine molecule has been used as a catalyst to reduce activation energy of CO₂ reduction reaction. It has been reported that CO₂ is reduced by pyridine catalysts at low overpotential around -0.58 V vs. SCE. Poly(4-vinylpyridine), which has pyridine functional groups shows similar catalytic properties to reduce CO₂ at low overpotential likes pyridinium catalysts. Different thickness of P(4-VP) coated Pt electrodes were analyzed to figure out catalytic properties for CO₂ reduction. Cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy methods showed catalytic CO₂ reduction properties of P(4-VP)/Pt electrode. Thin P(4-VP)/Pt film showed low current density of -0.16 mA/cm² under CO₂ atmosphere and the current density reached -0.45 mA/cm² with increase of P(4-VP) thickness. The increase of current density was explained by increased surface concentration of adsorbed pyridinium groups of thick P(4-VP) layer. Nyquist plots also showed decrease of impedance with increase of P(4-VP) layer indicating fast charge transfer between Pt and P(4-VP) layer due to increase of hybrid ionic complex formation on Pt surface. But charge transfer is restricted when P(4-VP) layer becomes more thick because of slowed protonation of pyridine groups adjacent to Pt surface due to suppressed permeability of electrolyte solution into the PVP membrane. This electrochemical observation provides new aspect of P(4-VP) polymer for CO₂ reduction.

1. Introduction

As global warming and energy depletion problems become significant, usage of fossil fuels should be suppressed because of exhaustion of fossil resources and emission of green-house gases. Therefore, substitution of fossil fuels to renewable, eco-friendly energy resources becomes one of the challenges nowadays. Conversion of CO₂ to useful hydrocarbon fuels has been attracted by many research groups in the reason of not only being alternative energy source instead of fossil fuels but also reducing emission of green-house gases.¹⁻³

Due to high reduction potential of CO₂ to CO^{•-} (-1.90 V vs. SHE) reaction known for the rate

determining step of CO₂ reduction, high overpotential is required for CO₂ reduction. The pyridinium electrocatalyst to overcome high overpotential of CO₂ reduction was reported for the first time by Bocarsly *et al.* using a hydrogenated palladium electrode in 1994.⁴ The total faradaic efficiency of CO₂ reduction to formic acid and methanol is observed as around 33 % by using pyridinium catalysts on hydrogenated Pt or Pd electrode.⁵ And the faradaic efficiency of methanol formation from CO₂ is observed nearly 100% by illuminated p-GaP semiconductor in aqueous system containing pyridinium catalysts.⁶⁻⁹ It has been known that pyridinium can lower the activation energy of CO₂ reduction by passing the carbamate species (PyCOOH⁰) intermediate instead of the CO⁻ pathway.^{10,11} Although the pyridinium can reduce the overpotential of CO₂ reduction reaction and showed considerable CO₂ conversion efficiency, the pyridine is known for its clastogenic, neurotoxic effects and can be harmful both animals and plants in aquatic environment. Moreover, pyridinium catalysts should be dispersed in electrolyte to play a role as catalysts for CO₂ reduction. So, it is difficult to separate the pyridinium catalysts and products of CO₂ reduction from the electrolyte solution. These drawbacks make the pyridine catalysts difficult to be utilized for the real application. So, for the large scale of application, it is required to develop both environmental friendly and immobilized types of catalysts for CO₂ reduction.

Herein, we report the catalytic properties of poly(4-vinylpyridine) [P(4-VP)] for CO₂ reduction reaction. P(4-VP) films were made by spin coating method on the Pt deposited fluorine doped tin oxide (FTO) substrate in different thickness. Electrochemical properties of each film were investigated by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedancespectroscopy (EIS). Finally, CO₂ reduction reaction was performed with P(4-VP)/Pt/FTO electrode and formaldehyde was detected as a primary product by GC. Thus this work gives new insight of utilization of P(4-VP) for CO₂ reduction to reduce activation energy of CO₂ molecule during reduction reaction process and possibility of being utilized as P(4-VP) electrode for artificial photosynthesis combined with photoanode.

2. Experimental

Chemicals. P-4VP (molecular weight ca. 160 000), sodium sulfate (99.0% anhydrous), formaldehyde (37-amine hydrochloride (99.0%)) were purchased from Sigma-Aldrich. Sodium hydroxide (97.0%) was acquired from DAEJUNG. Ethanol (99.9%) was received from EMD Millipore.

Preparation of P4VP/Pt films. Fluorine doped tin oxide (FTO) substrates were cleaned by sonication in mixture solution of 2-propanol, acetone and water (1:1:1, v/v/v). Platinum was coated by

sputtering on the FTO substrates for 45 sec. 1, 3, 5, 7, 9 wt% of P(4-VP) solutions were prepared by dissolving P(4-VP) in pure ethanol. P(4-VP)/Pt film was prepared by spin coating method, depositing P(4-VP) solution on Pt coated FTO substrate by 5000 rpm for 30s and heated in oven at 80°C for 6h

Electrochemical CO₂ reduction with P(4-VP)/Pt film. The electrochemical CO₂ reduction reaction was performed in two compartments of the electrochemical cell which is separated into anode and cathode parts (10 mL volume for each compartment). Before the CO₂ reduction reaction, 0.5 M Na₂SO₄ electrolyte was pre-purged by CO₂ for 30 min and pH was adjusted to pH5 by adding diluted NaOH solution. Cyclic voltammetry measurement (CV) and chronoamperometry (CA) during CO₂ reduction reaction experiments were performed by using a DY2300 series potentiostat of Digi-IVY in USA. Prepared P(4-VP)/Pt film, Pt foil, 3 M NaCl saturated Ag/AgCl electrode were used for working, counter and reference electrode, respectively. The area of working and counter electrode was 1.33 cm². During the CO₂ reduction reaction, CO₂ was purged continuously into the electrolyte by the flow rate of 10 sccm and injected directly to GC-TCD. The electrochemical impedance spectroscopy (EIS) measurement was conducted with the potentiostat (VSP, Biologics). The frequency was set from 0.1 Hz to 200 kHz at -0.6 V vs. Ag/AgCl and the amplitude was 20 mV.

GC measurement. 7890B series of GC-FID (Agilent Technologies) equipped with a DB-624 column (60 m x 250 μm x 1.4 μm) and Stratum Purge & Trap (TELEDYNE TEKMAR) was used to analyze products from CO₂ reduction reaction. Injector was operated at constant 200°C with a He carrier gas (1.5 mL/min). Oven temperature was held at 40 °C for 1 min and heated to 150 °C by 5 °C/min and the detector was operated at 250°C. The 5 mL of electrolyte samples containing salts were injected to purge & trap instrument. Injected samples were heated at 40 °C at the same time, nitrogen gas was purged to the electrolyte by 40 mL/min of purging rate.

7890A series of GC-TCD (Agilent Technologies) equipped with a Agilent 19095P-MS6 column (30 m x 530 μm x 25 μm) was used to detect hydrogen gas from CO₂ reduction reaction. Inlet was maintained at 200°C with a Ar carrier gas (3 mL/min). Oven was maintained at constant temperature of 50°C and the TCD detector was operated at 150°C.

3. Result and Discussion

Poly(4-vinylpyridine) (P(4-VP)) can be protonated by capturing protons from electrolyte at pH 5 condition (Fig. 1(a)). The protonated pyridine groups of P(4-VP) can have electrocatalytic properties for CO₂ reduction like pyridinium catalysts.^{12,13} The structure of P(4-VP)/Pt/FTO films was characterized by X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR). The XPS spectra of sputtered Pt layer on FTO substrate is shown in Fig. 1 (b).

In Pt 4f spectra, the binding energy of Pt 4f_{7/2} and Pt 4f_{5/2} was 71.5 eV and 68.2 eV, respectively. This binding energy is well matched with previous report on binding energy of metallic Pt, 71.1 eV and 67.8 eV for Pt 4f_{7/2} and Pt 4f_{5/2}, which means that the sputtered Pt layer exists in metallic Pt state.⁵ The deposited state of P(4-VP) was revealed by IR spectra in Fig 1. (c). The IR peak on 1600 cm⁻¹ and 1400 cm⁻¹ are derived from C=C stretch of aromatic pyridine ring of P(4-VP), which is well matched with previous reported IR spectra of p(4-VP).¹³ Considering above XPS spectra and IR spectra, the P(4-VP)/Pt/FTO electrodes are well constructed with maintaining own chemical traits. The thickness of P(4-VP) layer on Pt/FTO substrate was controlled by changing weight percentage of P(4-VP) in spin coating solution (Fig. 2). The thickness of P(4-VP) layer on Pt/FTO substrate was 170 nm, 260 nm, 350 nm, 520 nm and 830 nm for 1 wt% of P(4-VP) (Fig 2a), 3 wt% of P(4-VP) (Fig 2b), 5 wt% of P(4-VP) (Fig 2c), 7wt% of P(4-VP) (Fig 2d) and 9wt% of P(4-VP) (Fig 2e), respectively.

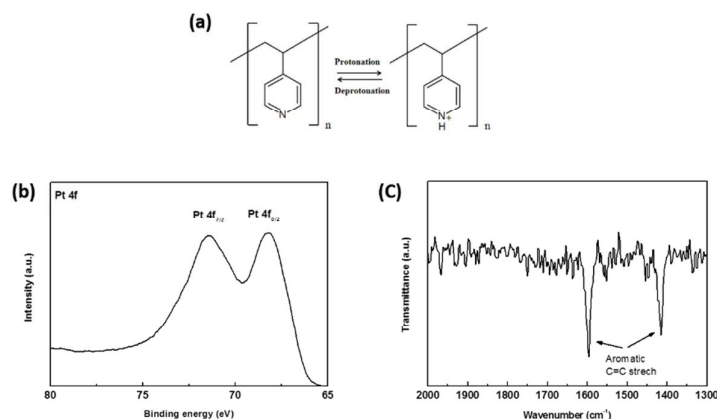


Fig. 1(a) Structural formulas of P(4-VP) (left) and protonated P(4-VP) (right). (b) Pt 4f XPS spectrum of sputtered Pt layer on FTO substrate. (c) IR spectrum of deposited P(4-VP) layer.

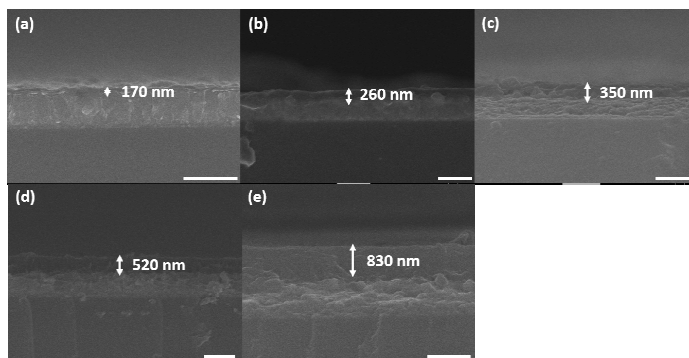


Fig 2. The cross sectional SEM image of P(4-VP)/Pt/FTO electrode. (a) 1 wt% of P(4-VP), (b) 3 wt% of P(4-VP), (c) 5 wt% of P(4-VP), (d) 7 wt% of P(4-VP), (e) 9 wt% of P(4-VP) (All scale bars are 1000 nm).

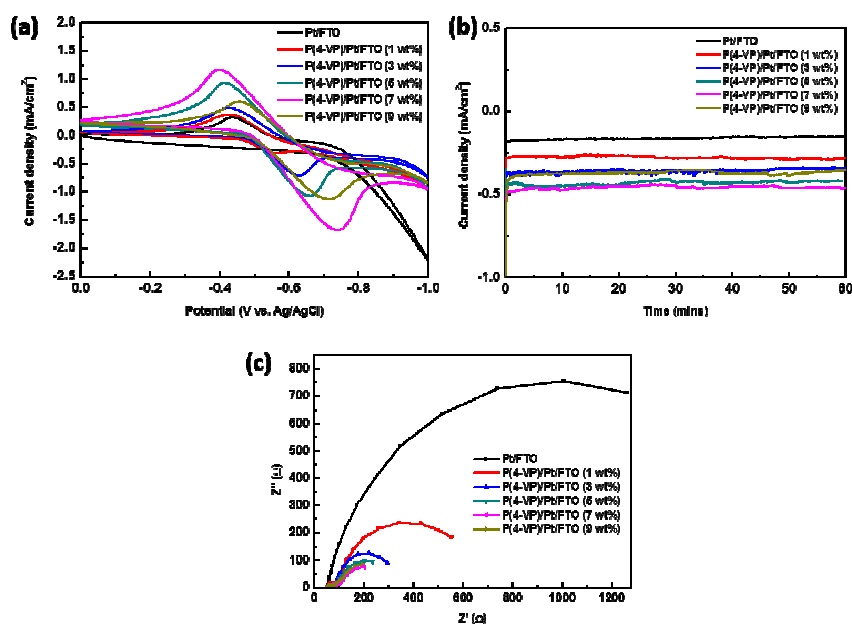


Fig 3.(a) Cyclic voltammety of Pt/FTO substrate and P(4-VP)/Pt/FTO electrode with in different concentration of P(4-VP). (b) Chronoamperometry of Pt/FTO substrate and P(4-VP)/Pt/FTO electrode with in different concentration of P(4-VP). (c) Electro impedance spectroscopy of Pt/FTO substrate and P(4-VP)/Pt/FTO electrode with in different concentration of P(4-VP).

Electrocatalytic properties of coated P(4-VP) film on Pt/FTO substrate was invested by electrochemical methods. All electrochemical analysis was conducted in CO_2 purged 0.5 M Na_2SO_4 solution with PH adjusted by diluted NaOH and HNO_3 solution in both CO_2 and Ar pre-purged electrolyte solution. Cyclic voltammograms (CV) measured for Pt/FTO electrode and P(4-VP)/Pt/FTO electrodes with different thickness of P(4-VP) layer are shown in Fig 3 (a). A reversible cathodic peak

was observed at P(4-VP) coated Pt/FTO electrode while bare Pt/FTO electrode did not show any cathodic peak. This means that a reversible cathodic wave of pyridinium catalysts is unique electrochemical feature on Pt surface. It has been reported by Batista *et al.* that pyridinium is reduced to pyridine by accepting one electron from Pt electrode forming adsorbed hybrid on Pt surface.¹⁴⁻¹⁶ Therefore, the reduction potential of pyridinium on Pt surface (-0.58 V vs. SCE) observed at cyclic voltammetry is related with protons transfer between pyridinium and Pt surface by exchanging one electron. Likewise the pyridinium molecules, the reduction potential of cathodic wave of P(4-VP) was observed around -0.65 V vs. Ag/AgCl reference electrode on Pt surface. So it can be demonstrated that cathodic peak observed with P(4-VP) coated electrode indicates protons transfer from protonated pyridine groups of P(4-VP) layer to Pt surface.¹⁴

The peak current density of P(4-VP)/Pt/FTO electrodes increased continuously from the thin P(4-VP) film prepared by 1 wt% solution to the thick P(4-VP) film prepared by 7 wt% solution. But the peak current was decreased when the P(4-VP) layer became thicker in prepared by 9 wt% solution. The redox curves of cyclic voltammograms are related with adsorbed pyridinium functional groups of P(4-VP) film on Pt surface. Chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) measurement were conducted at -0.6 V vs. Ag/AgCl in CO₂ saturated 0.5 M Na₂SO₄ electrolyte solution (pH 5). Fig 3(b) shows the i-t curves in CA of Pt/FTO electrode and P(4-VP)/Pt/FTO electrodes with in a different thickness of P(4-VP) layer. In i-t curves, the current value was maintained in stable value over 1 h, which means that all electrodes are stable and showed catalytic property during the whole reaction time. Pt/FTO electrode showed around -0.16 mA/cm² of current density and P(4-VP)/Pt/FTO electrodes showed the current values increased from -0.26 mA/cm² at 1 wt% of P(4-VP) layer to -0.45 mA/cm² at 7 wt% of P(4-VP) layer and decreased to -0.36 mA/cm² in 9 wt% of P(4-VP) layer. The decreased current value in 9 wt% of P(4-VP) layer is well matched with previous CV results. The Nyquist plots of Pt/FTO and P(4-VP)/Pt/FTO electrode which measured at -0.6 V vs. Ag/AgCl in CO₂ purged 0.5 M Na₂SO₄ in pH5 showed in Fig 3(c). Two distinguishable semicircles were observed at P(4-VP)/Pt/FTO electrode whereas one semicircle was observed at Pt/FTO electrode, which indicating resistance of charge transfer from Pt to electrolyte. First small semicircles correspond to resistance of P(4-VP) and the second semicircle is related with charge transfer from Pt to P(4-VP) layer. In contrast with Pt/FTO electrode surface, pyridinium groups of P(4-VP) layer can provide Pt-H hybrid on Pt surface at low potential, leading facile charge transfer for CO₂ reduction.¹⁴ Second semicircles, which derived from P(4-VP)/Pt interface showed similar tendency with previous CV and CA experiments, decreased as the thickness of P(4-VP) layer until 7 wt% of P(4-VP) and increased as the thickness of the P(4-VP) layer getting thick. Decrease of impedance value means that fast charge transfer occurred through the membrane of P(4-VP) layer on Pt interface to

the electrolyte solution.¹⁷

The concentration of adsorbed species (Γ_{ads}) on electrode surface can be calculated by following eq(1), where i_p is peak current, F the faraday constant, A the surface area of the electrode, v the scan rate, R the gas constant and T the absolute temperature, respectively.

$$i_p = F^2 A \Gamma_{\text{ads}} v / 4RT \quad (1)$$

The calculated concentration of pyridinium groups of P(4-VP) layer reached from $1.7 \times 10^{-8} \text{ mol/cm}^2$ at P(4-VP) film prepared by 1 wt% solution to $8.9 \times 10^{-8} \text{ mol/cm}^2$ at P(4-VP) film prepared by 9 wt% solution (Table 1). The increased current from P(4-VP)/Pt/FTO electrode with different thickness of P(4-VP) layer can be explained by increased concentration of adsorbed pyridinium groups of thick P(4-VP) layer.

But when the P(4-VP) layer became more thick, the concentration of adsorbed pyridinium groups decreased to $5.9 \times 10^{-8} \text{ mol/cm}^2$. The poly(vinylpyridine) polymer has been known about its ion-exchange ability forming positive charge on pyridine groups by accepting protons from electrolyte at acidic condition (under pH 5.5).^{18,19} So under acidic condition, pyridine groups adjacent to Pt surface forms pyridinium groups by accepting protons from permeated electrolyte.

P(4-VP) thickness (nm)	Surface concentration (mol/cm ²)
150	1.7E-08
260	3.7E-08
350	5.6E-08
520	8.9E-08
830	5.9E-08

Table 1. Table of calculated concentration of pyridinium groups in different thickness of P(4-VP) layer.

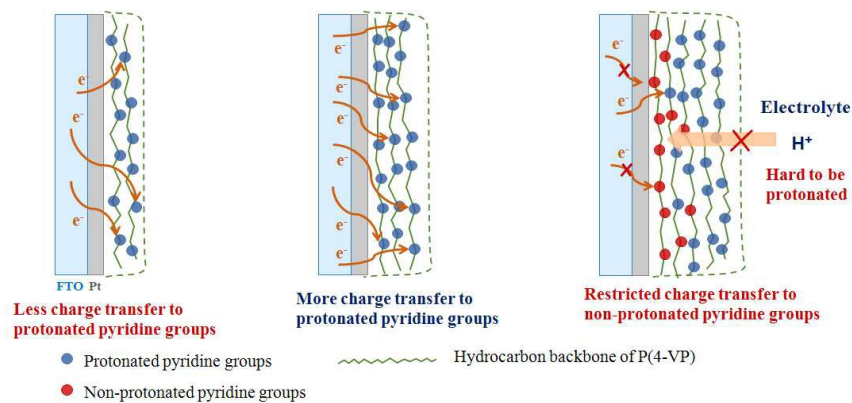


Fig 4. Schematic drawings of electron transfer from Pt to pyridinium groups of P(4-VP) layer in difference thickness.

On Pt surface, the pyridinium groups of P(4-VP) are reduced to pyridine groups by accepting electrons from Pt electrode making the P(4-VP) film equilibrated to protonated and deprotonated state. If the P(4-VP) layer becomes too thick, electrolyte solution cannot easily permeate through the thick P(4-VP) layer. Consequently, the rate of deprotonation of pyridinium groups becomes faster than protonation of pyridine groups. pyridine groups which are adjacent to Pt surface cannot easily accept protons from electrolyte solution. Consequently, the low concentration of adsorbed pyridinium groups of P(4-VP) on Pt surface inhibits charge transfer between Pt and P(4-VP) layer, leading low current which shown in CV and CA. Of course non-protonated pyridinium group will have low dielectric constant of the membrane media, which will cause the high impedance and low proton conductivity.

The scheme for electron transfer between Pt and pyridinium groups of P(4-VP) is shown in Fig 4. In Fig 4, the green lines indicate backbones of P(4-VP) layer and the blue and red circles indicate protonated and non-protonated pyridine groups of P(4-VP), respectively. The adsorbed Pt-H hybrid, which comes from pyridinium reduces CO₂ through a protons-coupled-hybrid-transfer (PCHT).¹⁴⁻¹⁶

Based on this report, increased concentration of pyridinium groups of P(4-VP) means increase of active sites for CO₂ reduction on Pt surface. When the P(4-VP) layer is too thin, the concentration of adsorbed pyridinium is low, which means lack of active sites for CO₂ reduction while Increased P(4-VP) thickness provides higher surface concentration of adsorbed pyridinium groups on Pt surface.

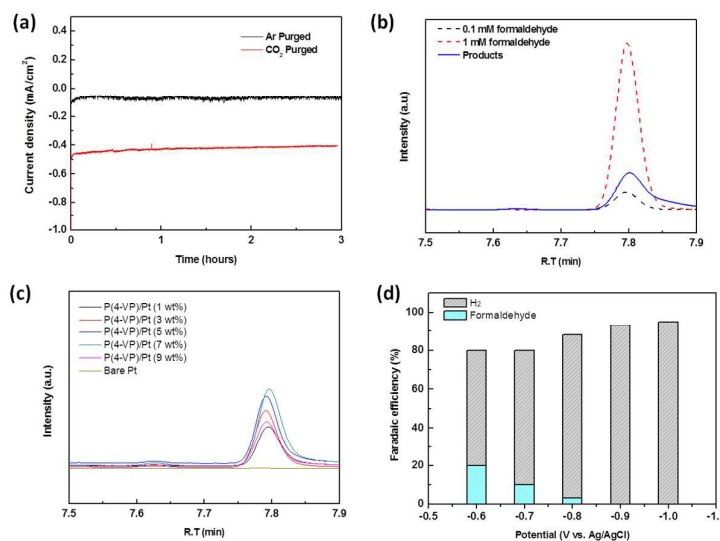


Fig 5. (a) i-t curve during reaction with P(4-VP)/Pt/FTO electrode in Ar purged in electrolyte and CO₂ purged in electrolyte. (b) GC analysis of produced CO₂ reduction product with P(4-VP)/Pt/FTO electrode. (c) GC analysis of produced CO₂ reduction product with P(4-VP)/Pt/FTO electrode within different thickness of P(4-VP) layer. (d) faradaic efficiency of products from CO₂ reduction.

Therefore, charge transfer between Pt and P(4-VP) layer becomes faster than when P(4-VP) layer is thin. But, when P(4-VP) layer becomes too thick, the rate of protonation is relatively slower than deprotonation causing restricted charge transfer to non-protonated pyridine groups because electrolyte solution cannot easily permeate through the thick P(4-VP) layer.

Based on above results, the CO₂ reduction reaction has performed with P(4-VP)/Pt/FTO electrodes in different P(4-VP) thickness. The current density during CO₂ reduction reaction is shown in Fig. 5(a), compared with Ar purged condition. The current density was increased in CO₂ purged electrolyte which means that pyridium groups in P(4-VP) react with CO₂ molecule and leading the reduction of CO₂. After 3 h reaction, the produced CO₂ reduction products are qualified and quantified by GC-purge and trap. The produced CO₂ reduction product has 7.8 min of retention time, which well matched with retention time of formaldehyde standard (Fig 5(b)). The concentration of produced formaldehyde was calculated by calibration curve which was calibrated by peak area of standard concentration of formaldehyde. The produced amount of formaldehyde is 48 μM, 73 μM, 98 μM, 129 μM and 58 μM for 1 wt% of P(4-VP), 3 wt% of P(4-VP), 5 wt% of P(4-VP), 7wt% of P(4-VP) and 9wt% of P(4-VP), respectively. However, in Pt/FTO electrode, any CO₂ reduction products including formaldehyde were not detected (Fig 5(c)). The faradaic efficiency of produced formaldehyde reached around 20% at -0.6 V vs. Ag/AgCl. But the faradaic efficiency decreased rapidly when the applied potential increased over -0.6 V vs. Ag/AgCl. It can be demonstrated by competition with CO₂ reduction and hydrogen evolution at more negative potential. The onset potential of hydrogen evolution was observed at -0.7 V vs. Ag/AgCl on bare Pt surface by CVs (Fig 3a). So the hydrogen evolution is more favorable than P(4-VP) catalyzed CO₂ reduction at more negative potential and it consistent with increasing hydrogen evolution detected by GC (Fig 5(d)). The other results on the quantification of other products, reduction potential tuning, increasing proton conductivity with nafion layer and isotope labeling study will be reported in the following report. All of the results can be applied for the optimization of parameters for the artificial photosynthesis of photoelectrochemical and photochemical processes.

4. Conclusion

In this report, P(4-VP)/Pt/FTO electrode was fabricated within different thickness of P(4-VP) layer for CO₂ reduction reaction and the catalytic properties of P(4-VP) for CO₂ reduction reaction was investigated. By using CV, CA and EIS, we found the optimal thickness of P(4-VP) layer for CO₂ reduction is around 520 nm. In 520 nm thickness, P(4-VP) layer showed the best properties for electron- proton coupling transport during CO₂ reduction reaction due to the pyridinium groups existing in the P(4-VP) layer. Finally, CO₂ reduction reaction was performed with P(4-VP)/Pt/FTO

electrode via electrochemical process and formaldehyde was detected as a primary product with 0.13 mM for 3 h reaction. The faradaic efficiency of formaldehyde reached to 20% at -0.6 V vs. Ag/AgCl but decreased at more negative potential due to competition with hydrogen evolution. Thus this work confirmed that P(4-VP) can be one of the candidate materials for CO₂ reduction at low overpotential and gives new insight on P(4-VP) as a supporting material for artificial photosynthesis system if the P(4-VP) is combined with other photocatalytic semiconductors. Furthermore results on the artificial photosynthesis by the optimized parameters for CO₂ reduction reaction will be reported in the following report.

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