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Photoelectrochemical CO_2 conversion system with 3C-SiC photo-anode and Pt counter electrode.

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Abstract

Photoelectrochemical (PEC) carbon dioxide (CO_2) conversion system is investigated by using 3C-SiC photo-anode with Pt counter electrode. Conduction band-edge of 3C-SiC is more negative than the potential for driving CO_2 reduction. It means that light-induced electron-hole pairs in the 3C-SiC have sufficient energy for CO_2 reduction. Under only solar-light illumination, a photo-current of 2.5 μA/cm^2 is flowed through this two-electrode system with showing photo-response. Finally, we confirmed the reaction products such as carbon monoxide (CO) and methane (CH_4) gases from CO_2 reduction reaction with hydrogen (H_2) gas generated by water-splitting.

1. Introduction

Carbon dioxide (CO_2) is considered as a greenhouse gas with drastic increasing over decades. In the different view point, however, CO_2 is an abundant carbon resource which is transformable into useful chemicals. CO_2 can be reduced electrochemically to formic acid (HCOOH), carbon monoxide (CO) and methane (CH_4) etc. In order to realize the energy conversion system, many efforts have been investigated [1-3]. As one of these efforts, the utilization of inorganic photo-electrode for artificial photosynthesis is on the focus to achieve the purpose. This technique has been rapidly developed since the demonstration of TiO_2 photo-electrode for hydrogen (H_2) gas generation [4]. However, there have been a few materials for the photo-electrode satisfying the condition of CO_2 reduction [2-3]. Here, 3C (Cubic) type SiC has been reported as good candidate for photo-anode. It has a proper band-gap of 2.3 eV to absorb solar-light efficiently. However, it has been mostly considered about water-splitting previously despite of its potential to solar-driven CO_2 reduction [5-6].

In this research, we demonstrated the 3C-SiC photo-anode for CO_2 reduction with Pt counter electrode system by confirming conduction band-edge potential, photo-response and reaction products.

2. Experiments

As the photo-anode, n-type 3C-SiC wafers were fabricated by low pressure chemical vapor deposition (LPCVD) on the Si substrate and separated by removing Si substrate. Here, 3C-SiC is doped by nitrogen in a density of 1.0×10^{16} cm^{-3}. For the Ohmic contact, aluminum (Al) layer 2 μm in thickness is deposited on backside. A platinum (Pt) was utilized as a counter electrode. Photoelectrochemical (PEC) cell is separated to anode and cathode sides by an ion exchange membrane. Then, 0.1 M NaOH (pH =13.6) and 0.1 M $KHCO_3$ (pH = 8.5) electrolytes were used in cathode and anode sides, separately. As a light source, A 500 W Xe lamp which has the same spectrum with solar-light was used. Before electrolysis, the PEC cell was purged by nitrogen (N_2) gas for 10 min. Then, CO_2 gas was injected to the cathode part of PEC cell for 30 min, and it was sealed to collect the gas products during the PEC reaction. The photo-current during photo-electrolysis was measured by chronoamperometry method with potentiostat. Impedance measurement were implemented to obtain conduction band-edge of 3C-SiC in the frequency range from 0.1 Hz to 20 kHz. Moreover, produced gases were analyzed by gas chromatography after the PEC reaction.

3. Results and Discussion

We firstly investigated the band-structure of 3C-SiC regarding CO_2 reduction potential by impedance measurement. Before calculation of the position of band-edge potential, flat-band potential, V_{fb}, for different pH 1.12, 8.36 and 12.84 was obtained by Mott-Schottky plots [4]. The band-edge potential is shown in Fig. 1. The conduction and valance band-edge is more negative and positive than H_2 evolving potential (H^+/H_2) and O_2 evolving potential (H_2O/O_2), respectively. Moreover, it is confirmed that the conduction band-edge is more negative than the potential level for producing formic acid (HCOOH) located at the highest level among materials produced by the CO_2 reduction regardless of the pH value.

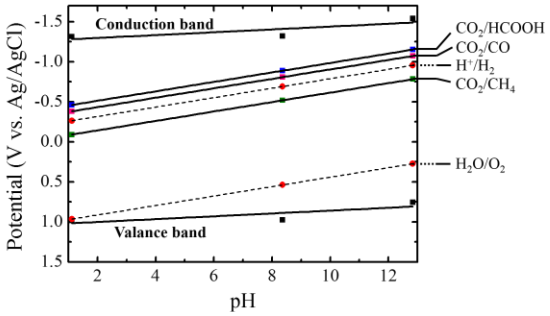

Fig. 1 Band-structure of 3C-SiC with regards to pH in comparison with potential level of water-splitting and CO_2 reduction.

Figure 2 shows the photo-response reaction of 3C-SiC photo-anode by switching light illumination. It was performed after CO_2 bubbling for 30 min in the condition of two-electrode connection between 3C-SiC photo-anode and

Pt counter electrode without an applied bias. A photocurrent of 2.5 μA/cm^2 was obtained by only light illumination through the system.

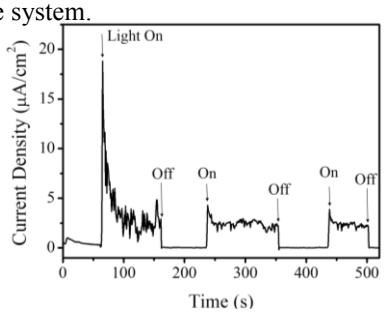

Fig. 2 Current density vs. reaction time. Light illumination is switched at interval of ~ 100 s to observe photo-response.

In order to observe the products from the CO_2 reduction, we analyzed the gases after the PEC reaction. Due to the insufficient photocurrent level without an applied bias, produced gases were collected during PEC reaction which shows a photocurrent of ~ 0.17 mA/cm^2 at a bias of 0.8 V (vs. counter electrode). Figure 3 shows the normalized collected gas production by total flowed charge (0.11 C). The main product is H_2 caused by water-splitting. In addition, CH_4 and CO of ~ 0.02 μmol/C are also obtained indicating the CO_2 reduction occurred in our system.

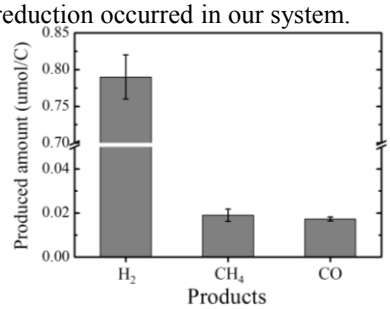

Fig. 3 Gas products as the result of the PEC reaction.

Next, we investigated the dependence of gas production on the charge amount by comparing at different flowed charges, 0.04, 0.09, 0.11, and 0.26 C. The sampling of the gases was implemented for 3 times. The linear relation between the H_2 production and charge amount is shown in Fig. 3(a). In Fig. 3(b), the CO gas increases to ~ 0.003 μmol at 0.09 C. However, it does not increase over 0.09 C and it even decreases to ~ 0.002 μmol at 0.28 C. The CH_4 gas shows similar tendency with the CO gas. The production is increased to ~ 0.0014 μmol at 0.11 C, but it considerably diminishes to 0.0008 μmol. This result indicates that no CO_2 reduction continues after ~ 0.1 C. This phenomenon might occur due to the property of the Pt electrode for strongly adsorbing the hydrogen ions [7]. Although CO_2 reduction occurs at the early phase of the reaction (< 0.1 C), hydrogen ions would cover the Pt electrode with time while suppressing the CO_2 reduction. It is expected that a copper (Cu) electrode reported as transition metal for CO_2 reduction would be better for this purpose [2-3].

3. Conclusion

The CO_2 conversion system with n-type 3C-SiC photo-anode and Pt counter electrode is investigated. The band-structure of 3C-SiC satisfies the potential level for the CO_2 conversion. The 3C-SiC photo-anode shows the photo-response with only illumination after CO_2 injection. As a result of the PEC reaction at 0.8 V, H_2, CO and CH_4 are generated. This result demonstrates 3C-SiC can be applied for the CO_2 reduction. While the H_2 gas is produced linearly with charge, the CO_2 reduction is suppressed after ~ 0.1 C, probably due to the largely adsorbed hydrogen ions on the Pt counter electrode. The use of a Cu electrode might improve the for CO_2 conversion with 3C-SiC.

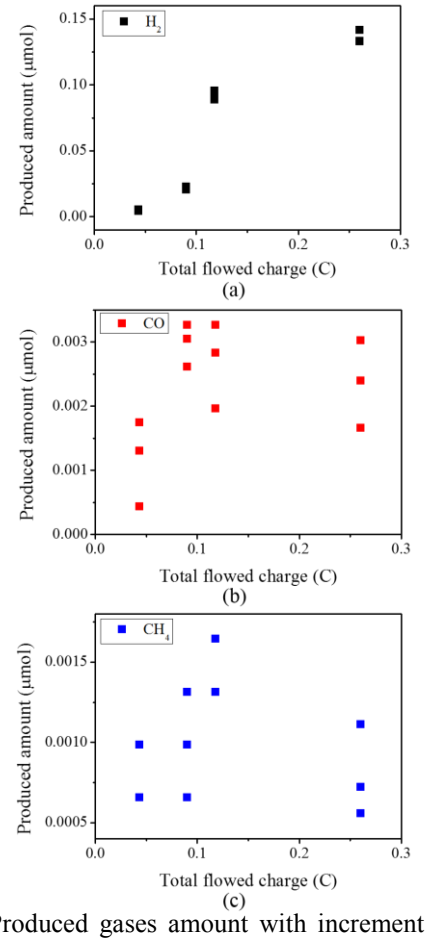

Fig. 4 Produced gases amount with increment of total charge. (a) H_2 (b) CO_2, and (c) CH_4.

Acknowledgements

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