

Enehanement of ethylene formation in electrochemical reduction of CO<sub>2</sub> at copper single crystal electrodes by introduction of step atoms to (100) basal plane

Y. Hori, I. Takahashi, O. Koga, and N. Hoshi  
 Department of Applied Chemistry,  
 Faculty of Engineering, Chiba University  
 Inage-ku, Chiba 263-8522, Japan

Methane, ethylene, and alcohols are uniquely produced at copper electrode in electrochemical reduction of CO<sub>2</sub> in aqueous electrolytes at ambient temperature (1). CO is intermediately formed in this process (2). We previously reported the electrochemical reduction of CO<sub>2</sub> at single crystal copper electrodes of low index planes (3). C<sub>2</sub>H<sub>4</sub> is formed more favorably than CH<sub>4</sub> on the (100) electrode, and CH<sub>4</sub> is predominantly produced on the (111) surface. Identical features are observed in the electrochemical reduction of CO. The present communication presents an extended work using various single crystal copper electrodes of high index planes. The electrocatalytic selectivity is significantly affected by the crystal orientation, and ethylene formation is enhanced by introduction of step atoms to (100) terraces.

Copper single crystals were prepared from 99.999% copper metal by Bridgeman method. After determination of the crystal orientation by X ray Laue back reflection method, the surface of the electrode was polished mechanically with diamond slurry, then electrochemically polished to mirror finish in concentrated phosphoric acid. Rinsed with ultra pure water, the electrode was transferred to the electrolysis cell with the electrode surface protected by a drop of slightly acidic ultra pure water (1 mM HClO<sub>4</sub>). The electrolyte solution 0.1 M KHCO<sub>3</sub> was purified by pre-electrolysis using a Pt black cathode overnight. The electrolyses were carried out at constant current density of 5 mA cm<sup>-2</sup> at the ambient temperature. The products were analyzed by gaschromatographs, a liquid chromatograph and a gas chromatograph-mass spectrometer.

The potential of zero charge (*PZC*) was determined by differential capacity measurements in 0.01 M KClO<sub>4</sub> solution. A linear correlation was obtained between the *PZC* and the broken bond density (*d<sub>bb</sub>*) (4), verifying the surfaces of the Cu electrode are correctly oriented.

CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and CO were produced as the gaseous products with small amount of H<sub>2</sub> formed in the competitive electrolysis of H<sub>2</sub>O. Ethanol, propanol, allyl alcohol, acetaldehyde, propylaldehyde, formic acid and acetic acid were detected as soluble products. The total current efficiency amounted approximately to 100%, and this fact verifies that the major products were accurately analyzed in the present experimental procedures. The product distribution was significantly affected by the crystal orientation.

(111) electrode gives rise to CH<sub>4</sub> formation with the current efficiency as high as nearly 50% at highly negative overpotential as shown in Fig. 1. Ethylene formation on (111) is less than 5%. The formation of CO is high in comparison with other crystal orientations. (111) surface of *fcc* crystals has low dangling bond density, or relatively stabilized. Thus the interaction of CO with (111) surface is not strong, and CO may easily be released from the electrode surface.

The (100) electrode is favorable in C<sub>2</sub>H<sub>4</sub> formation among low index planes. The formation of C<sub>2</sub>H<sub>4</sub>, aldehydes and alcohols is significantly activated by addi-

tion of (111) or (110) steps onto (100) basal plane. CH<sub>4</sub> formation is steeply decreased simultaneously. C<sub>2</sub>+ value, which includes C<sub>2</sub>H<sub>4</sub>, ethanol, propanol, allyl alcohol, acetaldehyde, propylaldehyde, and acetic acid, exceeds 70%. Figure 1 shows that introduction of (111) or (110) steps onto (100) terrace enhances the selectivity ratio C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> value in terms of current efficiency to 13 which is *ca.* 1 at (100) surface. The features of the introduction of (111) or (110) steps resemble each other. (100) terraces composed of 4 to 6 atomic rows are the most active in ethylene formation. Since C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> takes 0.1 at (111) surface, this value widely ranges more than 100 times.

The electrode potential of *n*(100) x (111) is nearly constant and relatively positive, -1.3 to -1.4 V vs. SHE as shown in Fig. 1, whereas the potential of *n*(100) x (110) tends to more negative value with the increase of step atom density.

Thus the crystal orientation of the electrode surface dramatically affects the product distribution, that is, the atomic configuration determines the reaction routes of the electrochemical reduction of CO<sub>2</sub>. We cannot reveal at present the mechanism how the atomic configuration is related with the electrocatalytic activity of the electrode surface and the reason why C<sub>2</sub>+ formation is activated by insertion of steps.

#### REFERENCES

- (1) Y. Hori, K. Kikuchi and S. Suzuki, Chem. Lett., 1985, 1695 (1985).
- (2) Y. Hori, A. Murata, and Y. Yoshinami, J. Chem. Soc., Faraday Trans., 87, 125 (1991).
- (3) Y. Hori, H. Wakebe, T. Tsukamoto and O. Koga, Surf. Sci., 335, 258 (1995).
- (4) A. Hamelin, J. Lecoer, Surf. Sci., 57, 771 (1976).
- (5) Y. Hori, R. Takahashi, Y. Yoshinami, and A. Murata, J. Phys. Chem., 101, 7075 (1997).

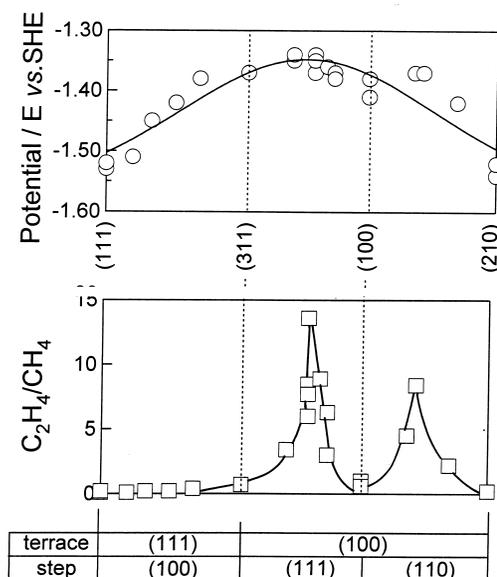


Fig. 1 C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> selectivity ratio given as a function of step atom density at Cu single crystal electrodes, *n*(111) x (100), *n*(100) x (111) and *n*(100) x (110) surfaces in the electrochemical reduction of CO<sub>2</sub>.