

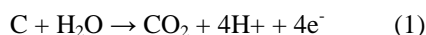
Investigation of influence of Pt oxidation state on carbon surface oxidation in PEMFC cathode electrode

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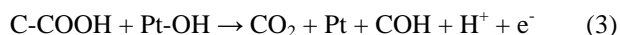
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The degradation of carbon in proton exchange membrane fuel cells (PEMFCs) electrodes has been reported as carbon corrosion recently under several fuel-cell operation procedures [1]. The influence of design factors for the membrane electrode assembly (MEA) and gas transport in the gas diffusion layer and the catalyst layer were often investigated at start up and partial hydrogen starvation. These results suggest that the coexistence of oxygen in the anode is critical for carbon corrosion on the positive electrode. Although the impact of carbon loss under ordinary fuel-cell operation is less than during startup and partial hydrogen starvation situations, it is estimated to be large enough to affect long-term durability [2]. Roen et al. [3] and Maass et al. [4] reported CO₂ generation on Pt/C catalyst in a PEMFC under potential dynamic condition such as cyclic voltammetry. They each suggested that platinum accelerated the oxidation of carbon supports under potential dynamic condition.

In order to elucidate the influence of platinum on carbon oxidation in more detail, carbon oxidation on Pt/C under potential dynamic model has been investigated. Two reactions were assigned as CO₂ generation reactions.



$$r_c = k_c \theta_c \frac{\exp\left(\frac{F}{RT}(\phi_1 - U_L^\theta)\right)}{1 + \exp\left(\frac{F}{RT}(\phi_1 - U_L^\theta)\right)} \exp\left(\frac{\alpha_{C,A} n_c F}{RT}(\phi_1 - U_c)\right) \quad (2)$$



$$r_{\text{CO}_2} = k_{\text{CO}_2} \theta_{\text{COOH}} \theta_{\text{PtOH}} \exp\left(\frac{\alpha_{\text{COHox},A} n_{\text{COHox}} F}{RT}(\phi_1 - U_{\text{CO}_2})\right) \quad (4)$$

The CO₂ generation and coverage of Pt and carbon surface species were calculated with these equations in Figure 1(a) and (b). It is estimated that CO₂ generation over 0.9 V is mainly governed by reaction (1) and simply depends on the cell potential. On the other hand, CO₂ generation under 0.9 V depends on both hydroquinone and OH adsorption on platinum and shows the local maximum around 0.8 V in Figure 1(b). It is well known that Pt-OH is oxidized with the increase in electrode potential and progress of Pt oxidation state reduces CO₂ generation. As Pt/C catalyst is often exposed around 0.8 V under fuel cell operation, carbon oxidation related with carbon surface group and platinum oxide species might affect fuel cell performance during life-time operation.

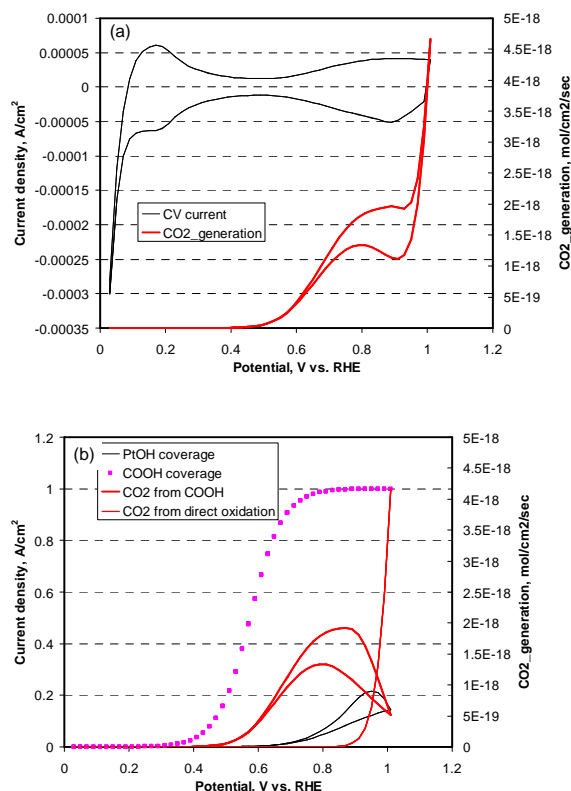


Figure 1. (a) Model calculation of cyclic voltammograms of Pt/C and CO₂ generation in PEMFC cathode electrode at 80 °C (b) model calculation of PtOH coverage, COOH coverage, CO₂ generation based on reaction (3) and CO₂ generation of reaction (1) under cyclic voltammogram.

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References

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