

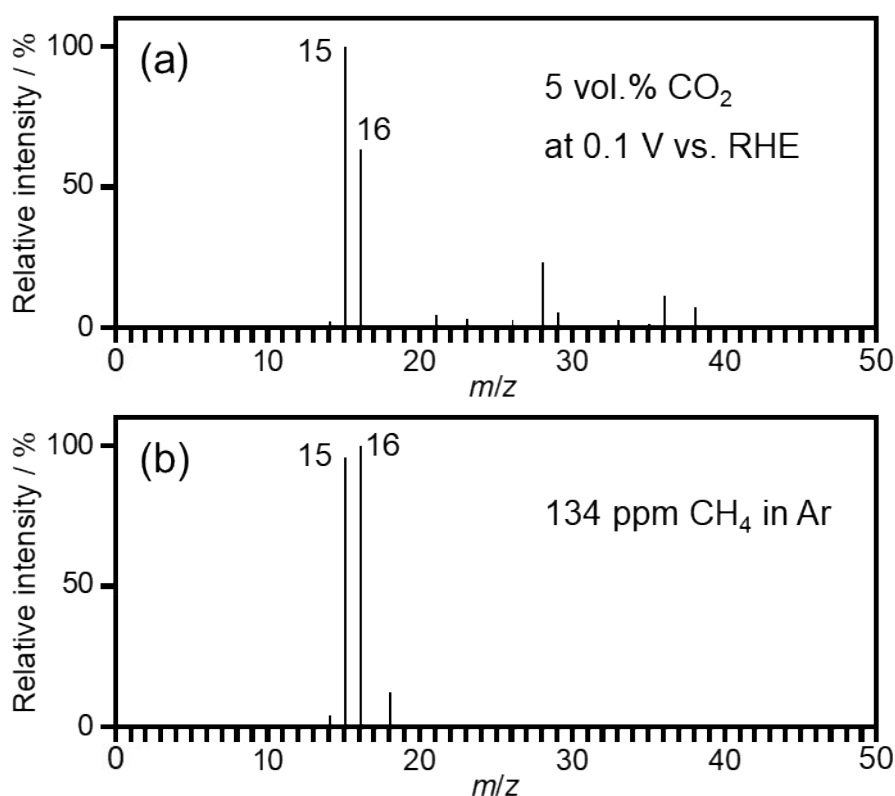
## Supplementary information

### Minimization of Pt-electrocatalyst deactivation in CO<sub>2</sub> reduction using polymer electrolyte cell

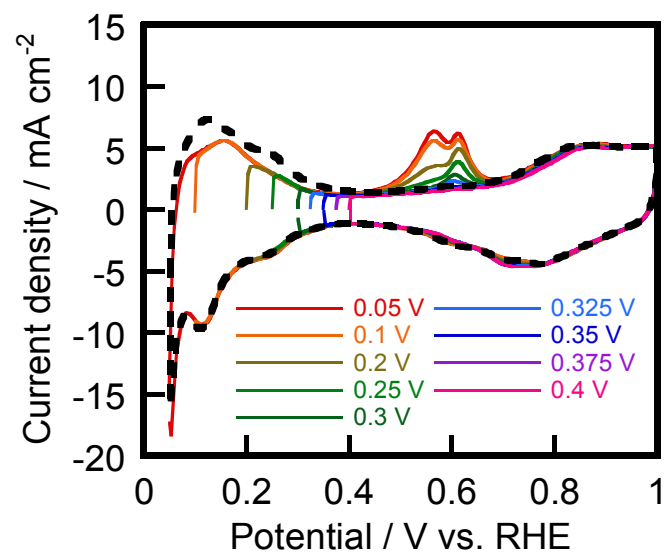
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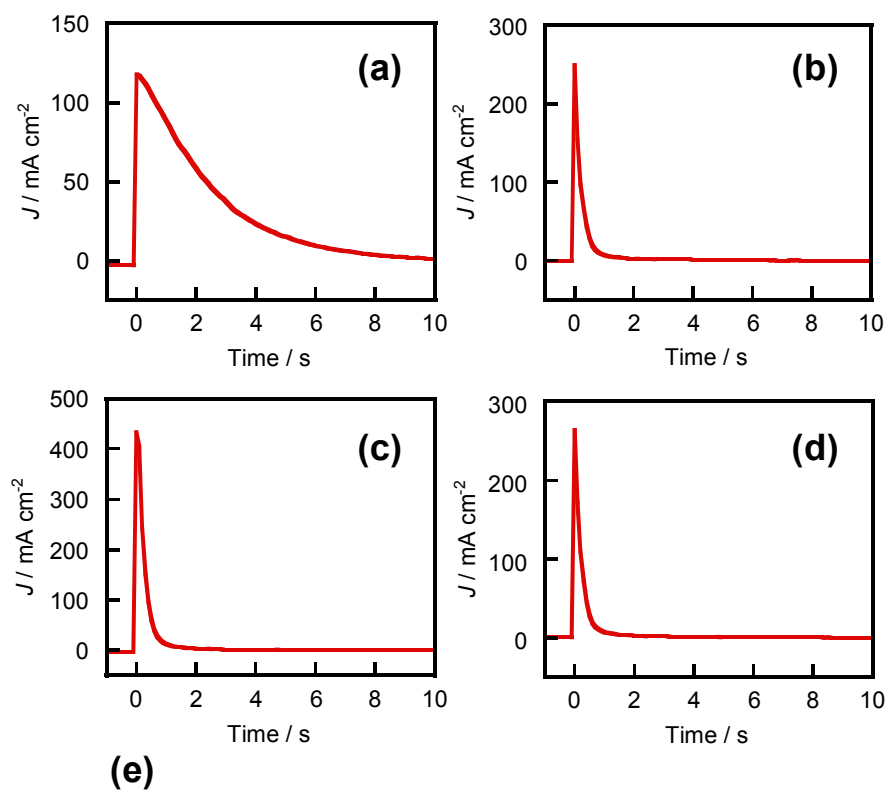
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**Fig. S1.** Mass spectra of (a) the WE exhaust gas from CO<sub>2</sub> reduction at 5 vol.% CO<sub>2</sub> and (b) CH<sub>4</sub> gas (purity: 99.999%) diluted with Ar.



**Fig. S2.** Cyclic voltammograms of Pt/C electrocatalyst at each 5-min initial hold potential at the CO<sub>2</sub> concentration of 4 vol.%. Scan rate was 10 mV/s.



**Fig. S3.** (a-d) Current responses by potential step and (e) the molar Pt-CO/Pt-H ratio after the operation displayed in Fig. 7(c) and Fig. 5(b). To consider why the recovery for the potential-sweep method is as high as 86.0% (Fig. 7(c)), we evaluated the formation ratio of Pt-CO/Pt-H after the operation displayed in Fig. 7(c). After the deactivation operation presented in Fig. 5(b), the potential was swept on the anodic side up to 0.3 V and subsequently returned on the cathodic side to 0.2 V. Afterwards, the potential was stepped to 0.7 V in (a) and to 0.7 V via the potential step to 0.35 V (b). Hence, the coulombic charges of both H and CO desorption ( $Q_H$  and  $Q_{CO}$ ) can be determined from the observed oxidation current in (a), and the  $Q_{CO}$  can be determined from the oxidation currents in (b). The  $Q_H$  can also be calculated by  $\{(Q \text{ obtained from (a)}) - (Q \text{ obtained from (b)})\}$ . As a result, the Pt-CO/Pt-H ratio formed on the catalyst surface, which was calculated by taking into account the number of electrons for each oxidation reaction, was determined as 1:17. Therefore, the Pt-CO/Pt-H ratio was

restored up to 1:17 after the recovery operation of potential sweep presented in Fig. 7(c). Here, when the potential was stepped to 0.7 V in (c) and to 0.7 V via the potential step to 0.35 V in (d) soon after the deactivation operation displayed in Fig. 5(b), the Pt-CO/Pt-H ratio was determined as 1:2.2. Overall, the method provided in Fig. 7(c) would be energy saving and effective to regenerate CH<sub>4</sub> production because the Pt-CO and Pt-H ratio in Fig. 7(c) shows a value close to the initial ratio of 1:18 (presented by Fig. 5(a)).