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## Supplementary Material

### Effect of Alkyl Chain Length of Imidazolium Cation on the Electroreduction of CO<sub>2</sub> to CO on Ag electrode in Acetonitrile

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### Reference Electrode Calibration

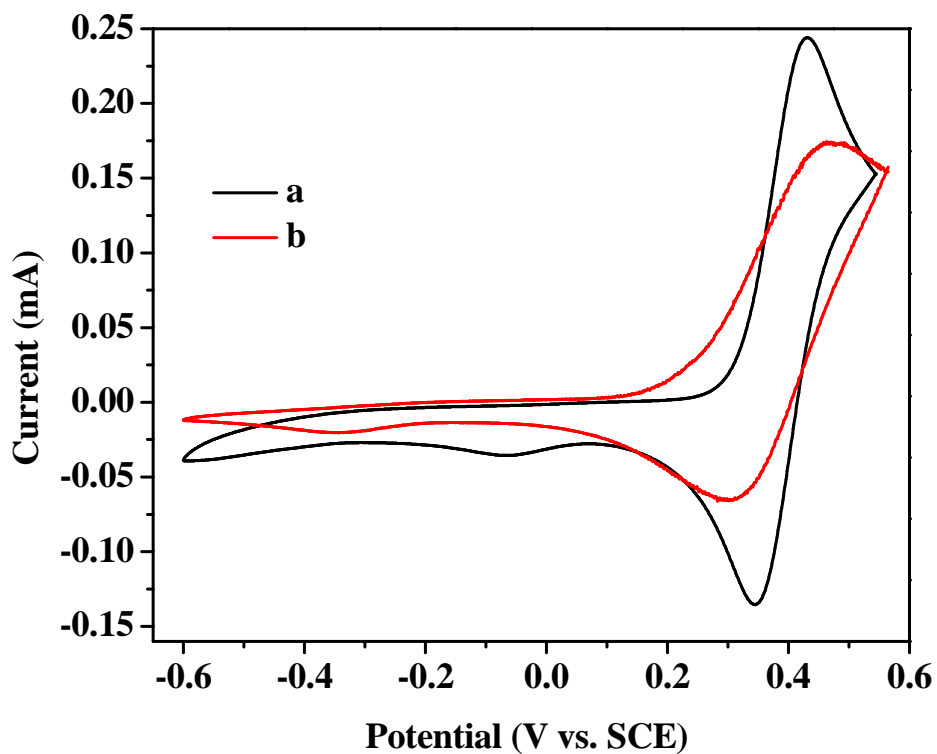
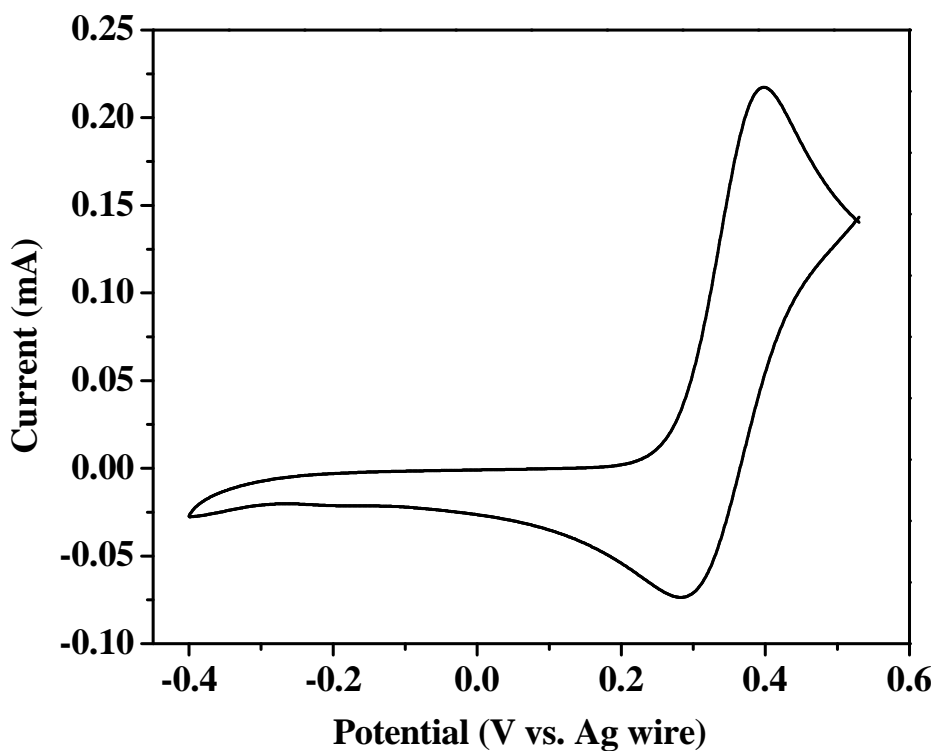


Figure S1: Anodic and cathodic waves for Fc at a scanning rate of 50 mV/s: (a) SCE in 0.1 M TBAPF<sub>6</sub>/AN with 0.5 M H<sub>2</sub>SO<sub>4</sub> as anolyte. (b) SCE in 0.1 M TBAPF<sub>6</sub>/AN with 0.1 M TBAPF<sub>6</sub>/AN as anolyte.



**Figure S2: Anodic and cathodic waves for Fc using Ag wire in 0.1 M TBAPF<sub>6</sub>/AN with 0.1 TBAPF<sub>6</sub>/AN as anolyte. at a scanning rate of 50 mV/s.**

The reference electrode calibration was based on the previous calibration of Pavlishchuk and Addison (1). Fig. S1 shows the ferrocene/ferrocenium (2.5mM) redox couple measured in acetonitrile using SCE reference electrode with 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M TBAPF<sub>6</sub>/AN as anolyte, respectively. Fig. S2 shows the redox couple measured in acetonitrile using Ag wire as reference electrode, respectively. E<sup>0</sup> (taken as the average of the peak potential of the anodic and cathodic wave) of the Fc<sup>+</sup>/Fc couple on Pt wire in AN was measured to be +38.9 mV vs. SCE in AN with 0.5 M H<sub>2</sub>SO<sub>4</sub> as anolyte and +38.2 mV vs. SCE with 0.1 M TBAPF<sub>6</sub>/AN as anolyte, compared to +38.0 mV reported by Pavlishchuk (1). We measured E<sup>0</sup> of the Fc<sup>+</sup>/Fc couple on Pt in AN vs. Ag wire to be +34.0 mV.

### ***Additional Reference***

- (1) V. V. Pavlishchuk, A. W. Addison, Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C *Inorg. Chim. Acta.* 2000, 298, 97-102.