

Communication

## New Insights Into the Role of Imidazolium-based Promoters for the Electroreduction of CO on a Silver Electrode

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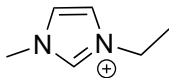
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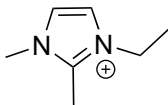
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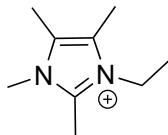
**1a:**  $\text{BF}_4^-$

**1b:** TFSI $^-$

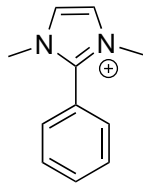
**1c:** OTf $^-$



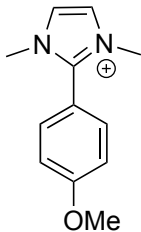
**2a:**  $\text{BF}_4^-$



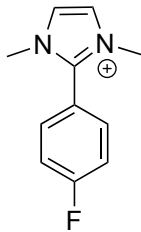
**3a:**  $\text{BF}_4^-$



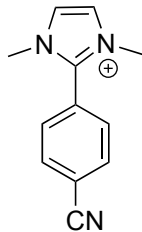
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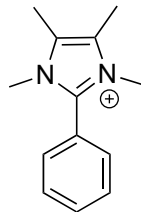
**5a:**  $\text{BF}_4^-$



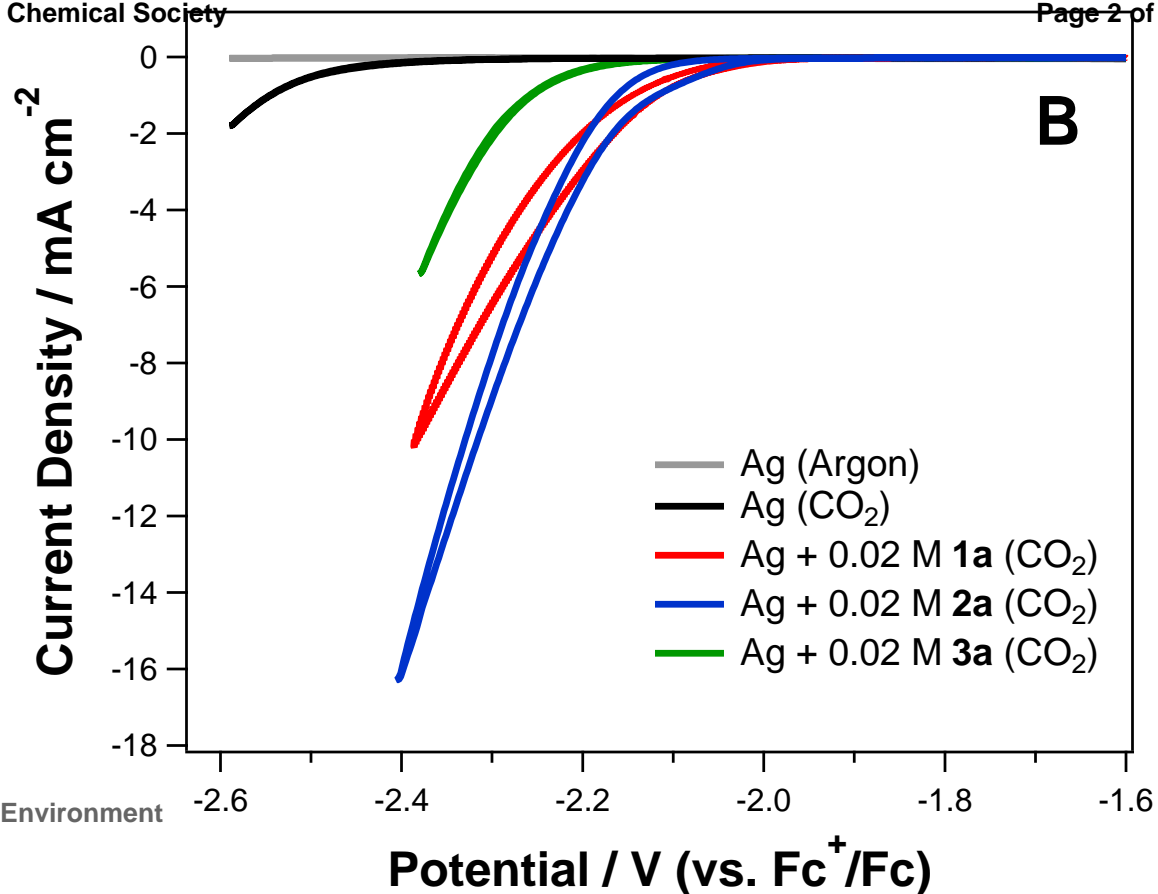
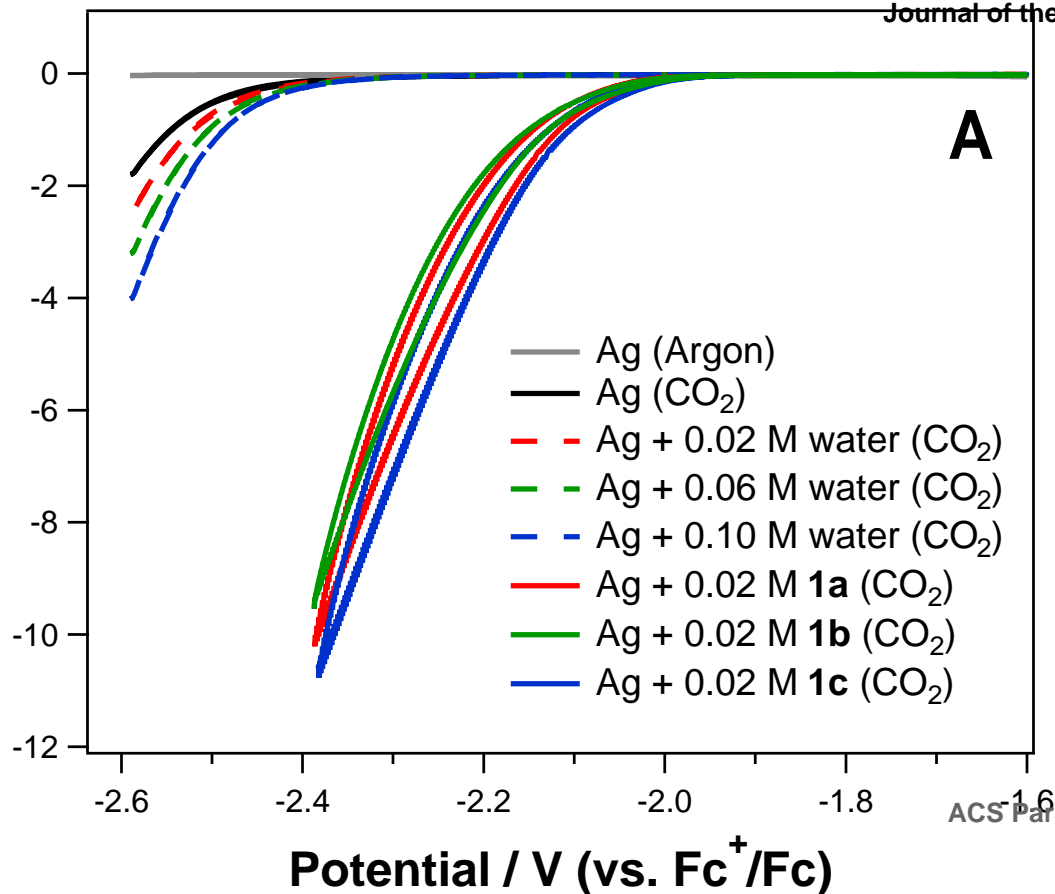
**6a:**  $\text{BF}_4^-$

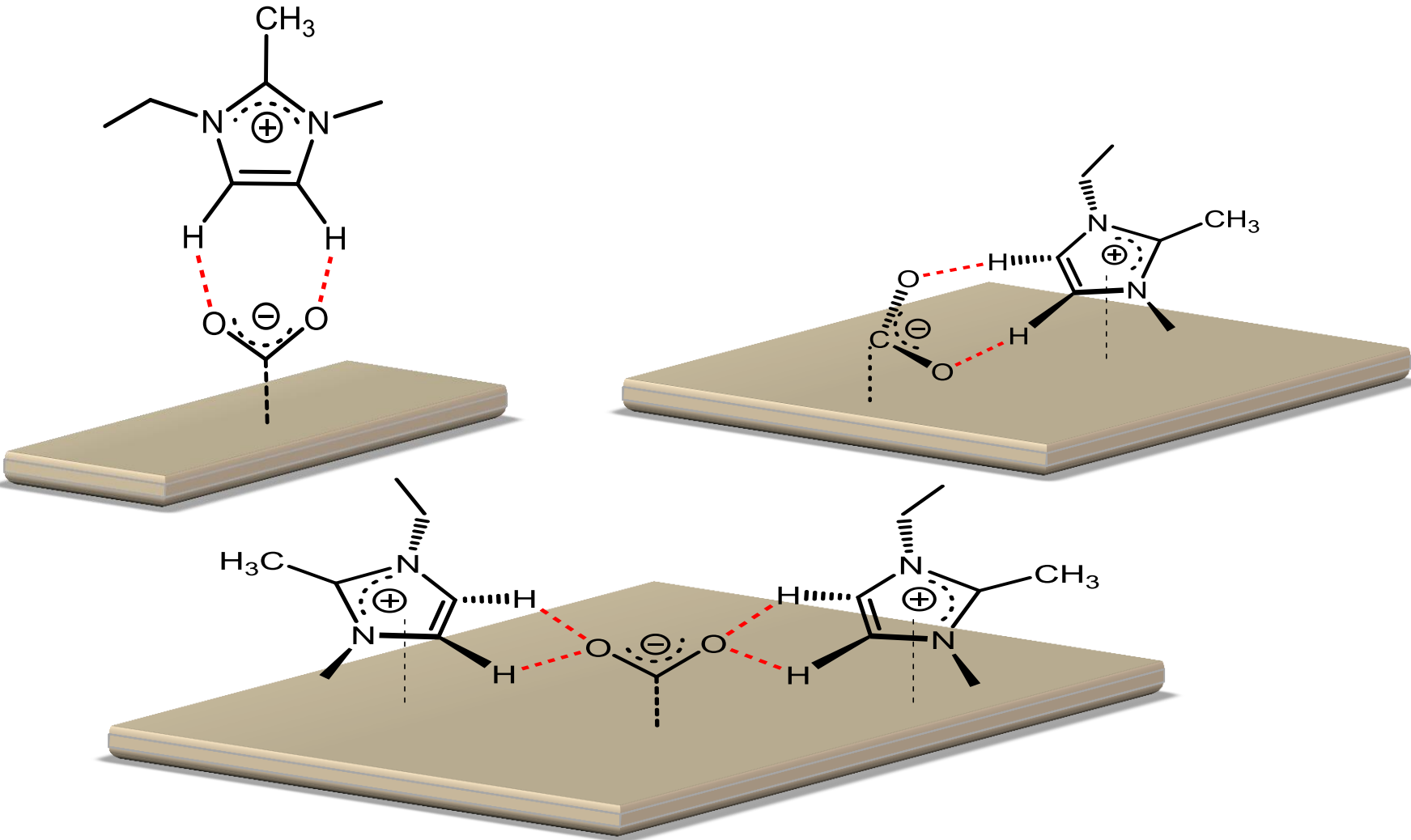


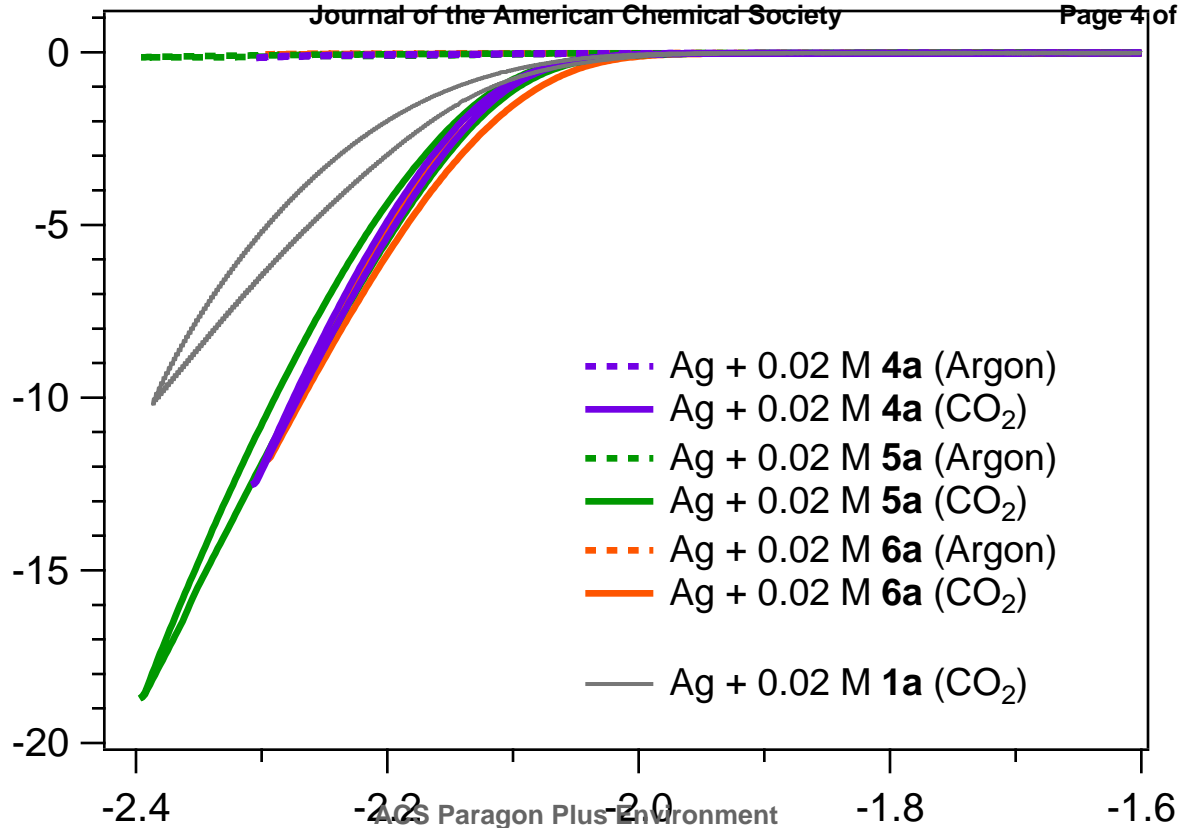
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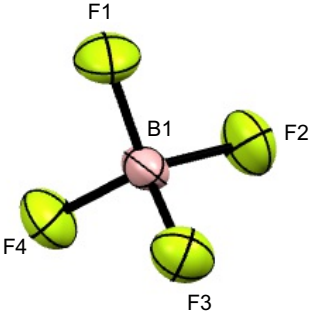
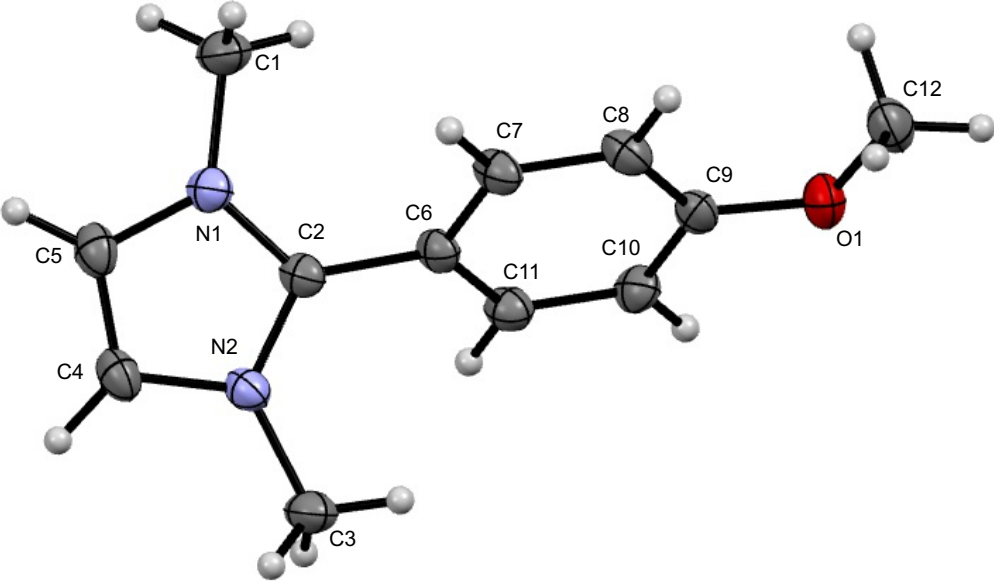


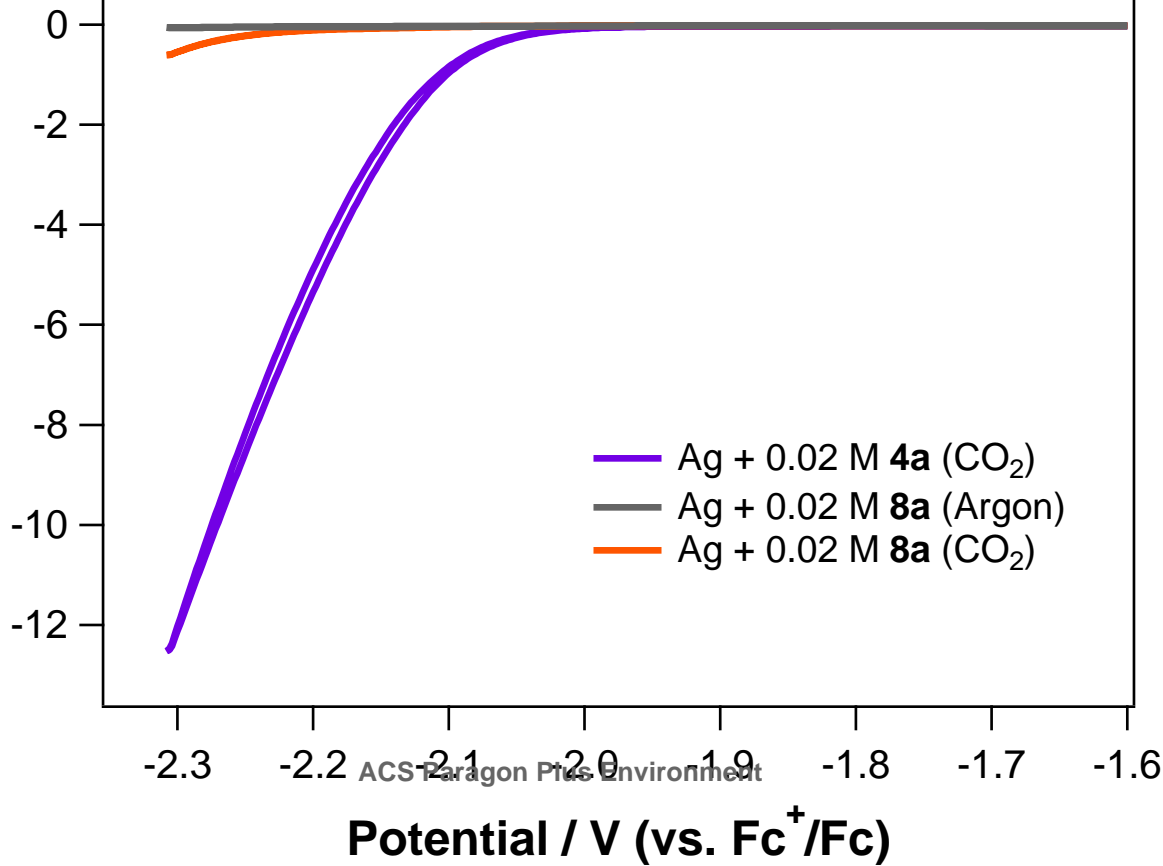
**8a:**  $\text{BF}_4^-$

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Current Density / mA cm<sup>-2</sup>Potential / V (vs. Fc<sup>+</sup>/Fc)



Current Density / mA cm<sup>-2</sup>

# New Insights Into the Role of Imidazolium-based Promoters for the Electroreduction of CO<sub>2</sub> on a Silver Electrode

Genevieve P. S. Lau,<sup>‡</sup> Marcel Schreier,<sup>‡</sup> Dmitry Vasilyev, Rosario Scopelliti, Michael Grätzel,\* Paul J. Dyson.\*

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## Supporting Information Placeholder

**ABSTRACT:** The electrochemical reduction of CO<sub>2</sub> to CO is a reaction of central importance for sustainable energy conversion and storage. Herein, structure-activity relationships of a series of imidazolium-based co-catalysts for this reaction are described, which demonstrate that the C4- and C5-protons on the imidazolium ring are vital for efficient catalysis. Further investigation of these findings led to the discovery of new imidazolium salts, which show superior activity as co-catalysts for the reaction, i.e. CO is selectively produced at significantly lower overpotentials with nearly quantitative faradaic yields for CO.

In addition to being a potent greenhouse gas, carbon dioxide is also widely recognized as an abundant and inexpensive C1 feedstock.<sup>1</sup> Therefore, highly selective and efficient methods for the recycling of carbon dioxide into fuels or chemicals are highly desirable, for both economic and ecological reasons. The electrochemical reduction of CO<sub>2</sub> to CO, ideally using renewable electricity, is an excellent example of such transformations, and would allow the twin objectives of carbon recycling and fuel production to be achieved.<sup>2</sup> Carbon monoxide is a key starting material for the synthesis of important commodities, such as acetic acid and methanol,<sup>3</sup> and is also frequently employed in the industrial synthesis of fine chemicals.<sup>4</sup> Moreover, CO can be further converted into liquid hydrocarbons via the Fischer-Tropsch process, yielding fuels that are directly compatible with existing energy infrastructure.<sup>5</sup>

It was recently shown that the addition of certain imidazolium-based ionic liquids, such as 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF<sub>4</sub>], resulted in a significant decrease in the overpotential required for the electrochemical reduction of CO<sub>2</sub> on silver electrodes.<sup>6</sup> Subsequently, this favorable effect was independently demonstrated by numerous groups,

and obtained in combination with a variety of electrocatalytic materials, including Ag,<sup>7a</sup> Pb,<sup>7b</sup> Sn,<sup>7c</sup> and Bi<sup>7d</sup> electrodes. The observed catalytic effect of these ionic liquid promoters has been studied by various groups in recent years,<sup>8a-g</sup> nevertheless there remain a number of open questions regarding their mechanism of action. Herein, a series of structurally related imidazolium-based salts are presented and evaluated as co-catalysts for the electrochemical reduction of CO<sub>2</sub>. Moreover, through the examination of structure-activity relationships, we show that the C4- and C5-protons on the imidazolium ring are crucial for catalysis.

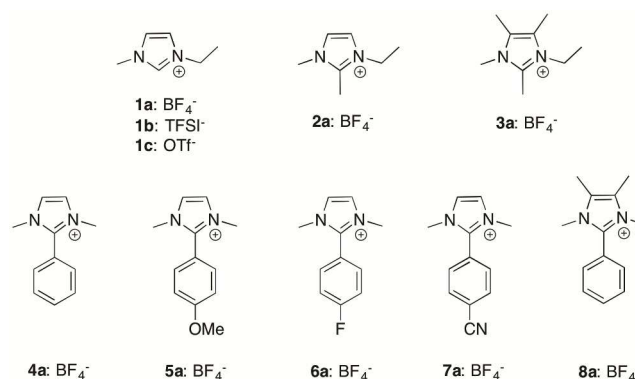


Figure 1. Structures of imidazolium salts studied.

The structures of all imidazolium salts used in this study are presented in **Figure 1**, and their catalytic performance was evaluated via cyclic voltammetry, in an undivided gas-tight electrochemical cell, with a standard 3-electrode set-up (unless otherwise stated). In all experiments, an Ag/AgCl quasi-reference electrode was employed, which was calibrated using the ferrocene/ferrocenium redox couple. The working electrode was a 3 mm diameter Ag disk electrode. A flamed platinum wire was used as the counter electrode, and the supporting electrolyte consisted of a 0.1M solution of tetrabutylammonium hexafluorophosphate [TBA][PF<sub>6</sub>]



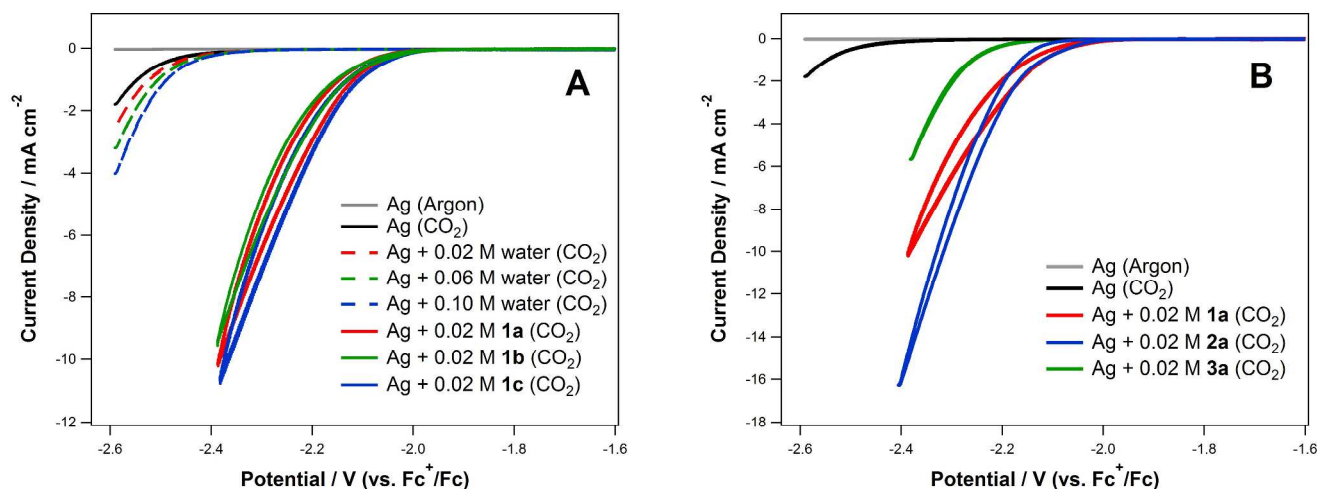


Figure 2. Cyclic voltammograms recorded for electrolytes containing different additives. (A) Effect of different anions and water concentrations on the electrochemical reduction of CO<sub>2</sub>. (B) Effect of different cations (**1a**, **2a**, **3a**) on the electrochemical reduction of CO<sub>2</sub>. Cyclic voltammograms recorded for electrolytes containing different additives (**1a-c**, **2a**, **3a**) in an argon-saturated environment are provided in the SI, Figure S1.

in anhydrous acetonitrile (7 mL). Prior to all electrochemical measurements, the imidazolium salts were dried for 15 mins at 120 °C, and the electrolyte was purged with argon for 15 mins to remove any dissolved oxygen. All voltammograms were recorded at a potential sweep rate of 100 mV/sec, in an air-conditioned room (22 °C). Full experimental details are provided in the SI.

It is well known that ionic liquids tend to be highly hygroscopic and may contain some residual water despite rigorous drying procedures.<sup>9</sup> The presence of water (a proton source) in the ionic liquid can potentially lead to enhanced reaction rates via proton-coupled electron transfer pathways.<sup>10a-b</sup> Our results show, however, that the effect of adding 0.02M of **1a** is markedly different from that of adding water at the same concentration, **Figure 2A**. This suggests that the observed catalytic effect of **1a** does not stem from residual water in the ionic liquid. Furthermore, the contribution of the anion was also found to be rather small, with compounds **1a**, **1b**, and **1c** exhibiting very similar catalytic behavior, **Figure 2A**.

Based on these findings, we turned our attention to the structure of the cation. Three different cations were investigated in the first instance, **1a**, **2a**, and **3a**, **Figure 2B**. Differences were observed in the catalytic activity of the three compounds, which decreased in the order **2a** > **1a** > **3a**. Numerous reports in the literature have suggested that the acidic proton at the C2-position of the imidazolium ring serves to stabilize a CO<sub>2</sub> anion radical intermediate via hydrogen bonding, and is therefore a key site for catalysis.<sup>11</sup> However, our results are not entirely consistent with this proposed model. Instead, it would appear that the proton at the C2-position is not in fact essential for catalysis, as a methyl group at this position resulted in even higher current densities (**2a**). Further methylation of the imidazolium ring (**3a**), how-

ever, resulted in a sharp decrease in catalytic activity, as well as a negative shift in the onset potential, **Figure 2B**. Taken together, these results show that the catalytic activity of these imidazolium salts is highly sensitive to the chemical structure of the cation. Since **3a** is the least effective co-catalyst (among compounds **1a-3a**), the C4- and C5- protons on the imidazolium ring appear to be critical. It can be expected that these protons play an important role in the stabilization of a CO<sub>2</sub> anion radical intermediate via hydrogen bond interactions. Taking into account existing hypotheses in the literature,<sup>7b</sup> we envision the following possible binding modes, **Figure 3**.

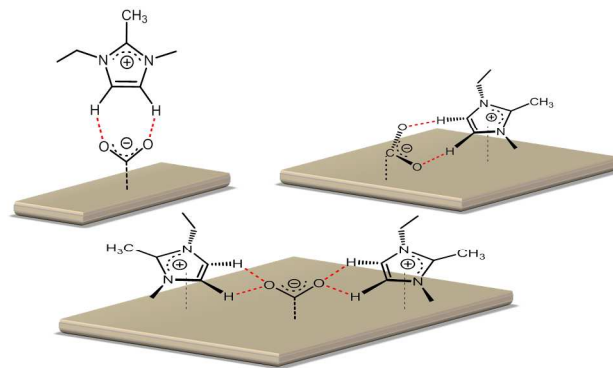


Figure 3. Possible binding modes of **2a** with an electro-generated CO<sub>2</sub> anion radical on a silver surface. Hydrogen bonds represented by dashed line (red).

In order to test this hypothesis, we sought to synthesize a range of imidazolium salts bearing substituents at the C2-position with different electronic properties, so as to modulate the strength of the proposed hydrogen bond interactions. Compounds **4a-6a** were selected and synthesized, and likewise evaluated via cyclic voltammetry. (Note: imidazolium salts with strong electron-withdrawing groups directly attached to the imidazolium

ring were found to decompose prior to CO<sub>2</sub> reduction, and were thus unsuitable for this study, Figure S2.)

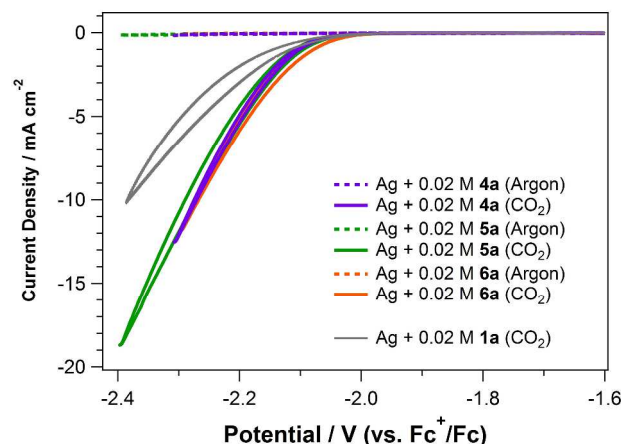


Figure 4. Cyclic voltammograms recorded for electrolytes containing **4a**, **5a**, or **6a**.

In general, the differences in the chemical structure of compounds **4a–6a** were found to have a negligible impact on their catalytic performance, resulting in very similar current responses, **Figure 4**. This result suggests that the different phenyl substituents are unable to significantly influence the electronic character of the C4- and C5- protons on the imidazolium ring. Such a behavior could be expected if the aromatic systems are not conjugated. Single crystal x-ray diffraction structures of **4a–6a** show that the imidazolium and phenyl rings lie on different planes, resulting in limited overlap of the  $\pi$  orbitals, **Figure 5**. In addition, the chemical shifts of the imidazolium protons in compounds **4a–6a** were found to be very similar, as determined by <sup>1</sup>H NMR spectroscopy, SI, and further indicates that their electronic properties do not differ greatly.

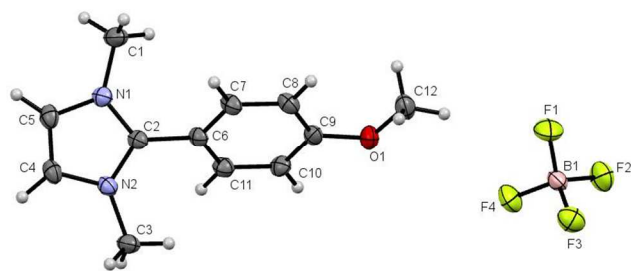


Figure 5. ORTEP plot of the crystal structure of **5a**. Selected bond (Å) and angles (°): N(1)–C(2), 1.338(2); N(1)–C(5), 1.375(2); N(1)–C(1), 1.464(2); N(2)–C(2), 1.344(2); N(2)–C(4), 1.378(2); N(2)–C(3), 1.465(2); C(4)–C(5), 1.342(3); C(2)–N(1)–C(5), 109.38(15); C(2)–N(1)–C(1), 126.32(15); C(5)–N(1)–C(1), 124.21(15); C(2)–N(2)–C(4), 109.37(15); C(2)–N(2)–C(3), 127.05(15); C(4)–N(2)–C(3), 123.51(15); N(1)–C(2)–N(2), 106.90(14); N(1)–C(2)–C(6), 127.14(15); N(2)–C(2)–C(6), 125.95(15). The structures of **4a–7a** are provided in the SI, Figure S5.

Furthermore, it is also interesting to note that the steric bulk of these phenyl substituents does not appear to

inhibit catalysis. Indeed, **4a–6a** displayed exceptional activity as co-catalysts, significantly exceeding that of the benchmark [EMIM][BF<sub>4</sub>] (**1a**) co-catalyst, under the same conditions, **Figure 4**. This again suggests that the C2- position is not the key site for CO<sub>2</sub> activation. Nevertheless, the different phenyl substituents had a remarkable impact on the cathodic limit of the imidazolium compounds. For example, compounds bearing electron-withdrawing substituents at the C2-position, **6a** and **7a**, were found to be more readily reduced, compared to their counterparts bearing electron-donating substituents, **5a**, Figure S3. In an argon-saturated environment, none of the imidazolium salts evaluated showed significant current flow prior to their respective cathodic limits, **Figure 4**. Under CO<sub>2</sub>, however, catalytic currents were observed at much more positive potentials, where the imidazolium cation is not yet reduced. This serves as a strong indication of the CO<sub>2</sub>-activating effect of the imidazolium salts, and points against them acting as an electron shuttle.

Since the electronic properties of the C4- and C5- protons on the imidazolium ring could not be modulated via different phenyl substituents at the C2-position, a different approach was adopted, leading to the synthesis of **8a** – an analog of **4a** with methylated C4- and C5- positions. In contrast to **4a**, a large cathodic shift in the onset potential for CO<sub>2</sub> reduction was observed when **8a** was employed in the electrolyte. This led to negligible catalytic activity in the working potential range, **Figure 6**. Beyond -2.3 V, reduction of **8a** starts to take place, which presumably leads to undesirable side reactions. The significant inhibition of catalytic activity with the loss of the C4- and C5- protons on the imidazolium ring appears to be consistent with our hypothesis that these protons are likely involved in the stabilization of the CO<sub>2</sub> anion radical intermediate. That this effect is less pronounced in the case of **3a** suggests that other binding modes, which do not involve the C4- and C5- imidazolium protons, may also exist and play a role, accounting for the residual catalytic activity of **3a**.

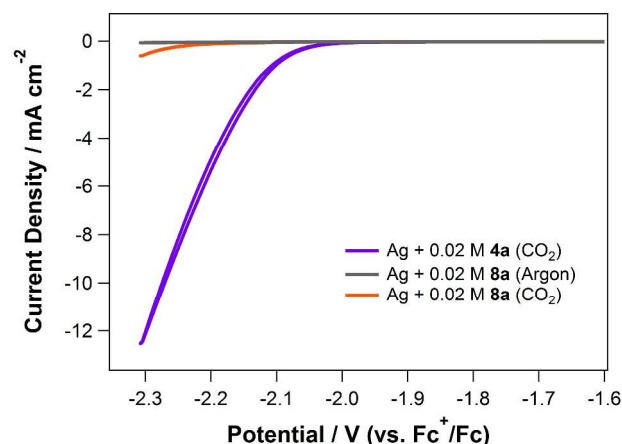


Figure 6. Cyclic voltammograms recorded for electrolytes containing **4a** or **8a**.

In order to verify that the irreversible reduction process observed on the voltammogram corresponds to the reduction of  $\text{CO}_2$ , preparative scale electrolysis was performed under galvanostatic conditions in the presence and absence of **4a**, with on-line gas sampling, see **Figure 7**. Similar experiments were also performed on compounds **1a–5a**, and the results are provided in the SI, along with full experimental details.

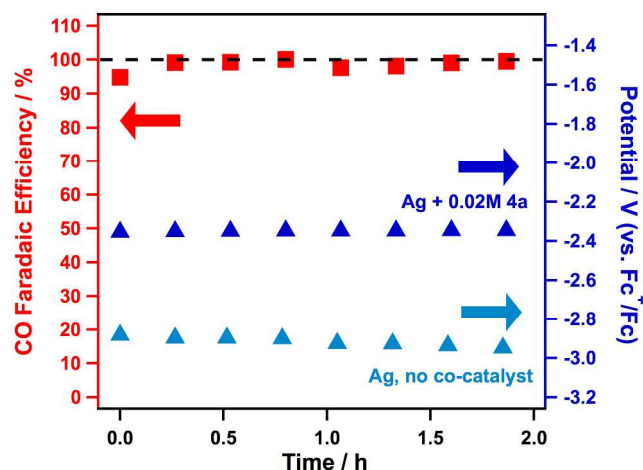


Figure 7. CO yields obtained with electrolyte containing 0.02M **4a** (red squares, left axis) and the operating potential required to maintain  $4.2 \text{ mA cm}^{-2}$  current density (dark blue triangles, right axis) over the course of 2 hours. To facilitate comparison, the operating potential required to maintain the same current density on a bare Ag electrode without co-catalyst **4a** is also shown (light blue triangles, left axis).

On-line gas sampling at regular intervals during the chronopotentiometry (CP) experiment showed CO as the only gaseous product formed during the reaction, with quantitative yields obtained for all the tested compounds. As can be seen in **Figure 7**, the addition of **4a** results in a substantial and sustained shift to a more positive operating potential required for maintaining the selected current density, thus demonstrating the efficacy of the co-catalyst. Importantly, high-resolution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic analysis of the post-electrolysis electrolyte showed no evidence for the degradation of **4a**, thus affirming its role as a co-catalyst in the reaction, Figure S4. While a number of different pathways have been reported, given the absence of changes to the imidazolium-based co-catalyst, as well as to  $\text{Bu}_4\text{N}^+$ , it is likely that  $\text{CO}_2$  serves as oxide acceptor in the reaction, yielding  $\text{CO}_3^{2-}$  as a by-product, Figure S4D.<sup>12</sup>

In summary, a series of structurally related imidazolium salts were prepared and evaluated as co-catalysts for the electrochemical reduction of  $\text{CO}_2$  on a silver electrode. It was found that the catalytic effect primarily originates from the cation, and that the protons at the C4- and C5-positions are essential for efficient catalysis. Furthermore, our investigations led to the discovery of a novel imidazolium-based co-catalyst, **4a**, that could

selectively produce CO with a higher activity than the well-established  $[\text{EMIM}][\text{BF}_4]$  co-catalyst. While the present study serves to highlight an important interaction between  $\text{CO}_2$  and the C4- and C5-protons of the imidazolium cation, it must be emphasized that other binding modes for the stabilization of the  $\text{CO}_2$  anion radical can be envisioned, and their contribution is likely to depend on the electrochemical system under investigation. It is hoped that these findings will serve as a basis for improved mechanistic understanding and lead to the development of even more efficient co-catalysts for this important reaction.

## ASSOCIATED CONTENT

**Supporting Information.** Full experimental details, synthetic procedures, NMR, and XRD data are included in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

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