Efficient electrochemical reduction of CO$_2$ to CO by “soft” functional materials

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Abstract: Electrochemical reduction of carbon dioxide (CO$_2$) to CO is a promising strategy. However, achieving high Faradaic efficiency with high current density using ionic liquids (ILs) electrolyte remains a challenge. In this study, the new ionic liquids (ILs) N-octyltrimethyl 1,2,4-triazole ammonium ([N$_{1118}$][TRIZ]) shows outstanding performance for electrochemical reduction of CO$_2$ to CO on the commercial Ag electrode, and the current density can be up to 50.8 mAcm$^{-2}$ with a Faradaic efficiency of 90.6%. The current density of CO is much higher than those reported in the ILs electrolyte. In addition, the density functional theory (DFT) calculation further proved that [N$_{1118}$][TRIZ] interact with CO$_2$ to form [N$_{1118}$]^+[TRIZ-CO$_2$] complex which played a key role in reducing the activation energy of CO$_2$. According to the molecular orbital theory, the electrons obtained from ILs was filled in the anti-bonding orbit ($\pi^*$) of the CO$_2$, resulting in reducing the C=O bond energy. This work provides a new strategy to design novel ILs for high efficiency electrochemical reduction of CO$_2$ to CO.

Keywords: ionic liquids; CO$_2$ reduction; electrolysis; carbon monoxide; density functional theory
1. Introduction

Carbon dioxide (CO₂), as one of most important greenhouse gases, is considered to be a non-toxic, inexpensive, renewable, and infinite C1-feedstock [1]. Converting CO₂ into useful products is considered as an important way towards CO₂ utilization [2]. An important conversion process is the reduction of CO₂ to CO. The product CO is promising as the main reactant of Fischer-Tropsch process [3]. Compared with traditional thermal reaction, the electrochemical reduction is a very promising strategy to convert CO₂ to CO under mild conditions by using hydro energy, solar and renewable wind [4, 5]. However, the reduction process faces a significant challenge mainly owing to large recombination energy in the transition of linear CO₂ to curved CO₂⁺ [6]. For this reason, certain electrolyte allowing for formation of complex with CO₂ would lower the reorganization energy for CO₂ activation [7].

As a ‘designer solvent’, room temperature ionic liquids (hereinafter referred to as ‘ILs’) are organic salts made up of anions and cations, which are liquids with temperature below 100 °C [8]. Recently, ILs have received much attention in the electrochemical reduction of CO₂ thanks to their properties of negligible vapor pressure, high CO₂ solubility, high electric conductivity and a wide potential window [9]. The ILs as promising cocatalysts have achieved impressive selectivity and yield in the electrocatalytic reduction of CO₂ to CO [10, 11]. Zhou et al. [12] presented that polycrystalline Ag cathode in ILs 1-butyl-3-methylimidazolium chloride ([EMIM]Cl) showed excellent synergy in electrochemical CO₂ reduction to CO with > 99% selectivity. Rosen et al. [6] reported that [EMIM][BF₄] could help to provide a low-energy pathway for the electrochemical reduction of CO₂ to CO by the formation of [EMIM-CO₂]---[BF₄] complex. Rudnev et al. [11] reported the combination of [BMIM][BF₄] with porous nanostructured silver foam catalyst produced a wide potential window of ~300 mV, where the Faraday efficiency of CO exceeds 94%. The electrocatalytic reduction of CO₂ to CO using [C₅mim][BF₄] ILs has been widely studied, however, the ILs containing [BF₄]⁻ anions are instable towards hydrolysis in contract with moisture, resulting in the formation of toxic and corrosive...
HF [13]. Meanwhile, the applicability of CO₂ reduction in imidazolium-based ILs is limited due to the low solubility of CO₂ [14]. At present, the above problems have been overcome by the use of ILs with 1,2,4-triazole as anion [7, 14]. The anion is able to chemically bind CO₂ to form [TRIZ-CO₂]⁻ complex resulting in high CO₂ solubility. However, the ILs are reported difficult to be synthesized. And to date, the use of ILs with 1,2,4-triazole as anion in electrochemical CO₂ reduction to CO has not been found. It is frequently encountered that the electrocatalytic CO₂ reduction to CO in ILs with satisfactory current density particularly have the electrodes made of commercial materials [15, 16]. Considering the above problems, herein, a new ILs N-octyltrimethyl 1,2,4-triazole ammonium ([N₁₁₁₈][TRIZ]) is designed and employed in electrocatalytic reduction of CO₂. [N₁₁₁₈][TRIZ] has been shown to have high CO₂ absorption capacity and is easy to be synthesized [17]. And the important feature of the [N₁₁₁₈][TRIZ] is the anion interact with CO₂ to form [TRIZ-CO₂]⁻ complex, thus reducing the activation energy of CO₂. It is particularly interested to discover whether the electrocatalytic CO₂ reduction with [N₁₁₁₈][TRIZ] ILs as cocatalyst can bring about satisfactory efficiency.

Therefore, to achieve high Faradaic efficiency with high current density using ionic liquids (ILs) electrolyte. In this study, a new ionic liquid [N₁₁₁₈][TRIZ] was synthesized by one-step method and used for the electrocatalytic reduction of CO₂. The effects of [N₁₁₁₈][TRIZ] concentrations and the water content on the electrocatalytic reduction of CO₂ with Ag as cathode were investigated separately through potentiostatic electrolysis. More importantly, the detailed mechanism of the electrochemical reduction of CO₂ in [N₁₁₁₈][TRIZ] ILs was investigated through density functional theory (DFT). This work aims to provide a new strategy to design novel ILs for high efficiency electrochemical reduction of CO₂ to CO.

2. Experimental section

2.1. Materials and ILs synthesis

1,2,4-Triazolysodium (TrizNa) and Trimethyloctylammonium chloride ([N₁₁₁₈]Cl) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Acetonitrile (AcN) was purchased from
Fuchen Chemical Reagent Store, Xing’an Market, Anci District, Langfang City. Ag (purity>99.99%) electrode with diameter 1.0 cm was purchased from Tianjin Aida Hensheng Technology Development Co. Ltd. Gaseous CO₂ was purchased from Beijing beiwen Gas Factory. Gaseous N₂, H₂, and CO were obtained from Beijing Chengxin Shunxing Special Gas Technology Co., Ltd.

\([\text{N}_{1118}][\text{TRIZ}]\) was synthesized by dissolving equimolar \([\text{N}_{1118}]\text{Cl}\) and TrizNa in ethanol and allowed to stir for 12 h under room temperature. The white solid was removed through a Buchner funnel, and the filtrate was evaporated to remove ethanol at 65 °C. The obtained yellow viscous liquid was placed in a vacuum oven and dried at 75 °C for 24 h. White solid precipitated out when CO₂ gas was passed into the light yellow ILs dissolved by AcN. The white solid was removed and AcN was removed by rotary evaporation of the filtrate at 75 °C. The obtained light yellow viscous liquid was dried in a vacuum oven at 75 °C for 48 h. The \([\text{N}_{1118}][\text{TRIZ}]\) was analyzed using \(^1\text{H}-\text{NMR}\) and \(^{13}\text{C}-\text{NMR}\) using Bruker ARX-600.

2.2. Electrochemical Measurements

The electrochemical data were recorded employing in CHI-660E (Shanghai CH instruments Co., China) with Ag plate as working electrode, platinum gauze as counter electrode, and \(0.01\ \text{mol L}^{-1}\ \text{Ag/Ag}^+\) (formed by dissolving AgClO₄ in 0.1 M TBAP-AcN) as reference electrode. Cyclic voltammograms (CV) experiments were recorded in stand three-electrode configuration with a sweep rate of 50 mV/s from -1.3 V to -3.0 V (vs. Ag/Ag⁺).

2.3. Product analysis of the electrochemical reactions

The electrochemical reactions were carried out at 293.15 K and atmospheric pressure in a H-type cell with Nafion 117 membrane separating the cathode and anode compartments. Prior to electrocatalysis test, the preparation consisted of polishing Ag electrode with sandpaper and rinsing with acetonitrile for more than 5 minutes. ILs was used as catholyte, and 0.1 M H₂SO₄ aqueous solution was used as anolyte. The catholyte was saturated by purging with CO₂ for at least 40 min before the CO₂ catalysis experiment. In order to mix better, the cathode solution was slight stirred while CO₂ gas was maintained at a speed of 60 ml min⁻¹. The gas products were collected using gas collecting bags and
then analyzed by Agilent 7890B gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) detector employing in N₂ as carrier gas. The definition of Faradaic efficiency (FE) was given in Eq. (1):

\[
FE = \frac{nF}{Q} \times 100\% 
\]  

(1)

Where \( n \) is moles of electrons required to reduce the CO₂ to the product, \( F \) stands for the Faraday constant (96485 C/mol), \( z \) refers to the number of electrons involved, and \( Q \) represents the total charge moved through the reaction process.

2.4. DFT calculations

All DFT calculations were performed via the Gaussian 09 program package [18]. The Becke’s three-parameter with Lee, Yang, and Parr’s (B3LYP) [19] hybrid functional was applied to perform geometry optimization between ILs and CO₂ with the 6-311+g(d,p) basis set [20]. Absence of negative frequencies confirmed that the optimized molecular structures are the minima.

3. Results and Discussion

3.1. Electrochemical characterization and product analysis

![Fig. 1. Structure of the [N_{1118}]^{+}[TRIZ]](image)

With superior performance of ILs electrolyte in mind, ILs composed of special functionalized anion are candidates for research owing the unique structure, as show in Fig. 1. The result of NMR of [N_{1118}]^{+}[TRIZ] showed that the synthesized ILs was consistent with the structure (Supporting Information, Fig. S1).
Fig. 2. CV curves with Ag electrode in the N$_2$-saturated and CO$_2$-saturated [N$_{1118}$][TRIZ]/AcN electrolyte.

A comparison of the cyclic voltammograms (CV) experiments were conducted to investigate the activity of [N$_{1118}$][TRIZ] (Fig. 2). The high viscosity of ILs is not conducive to the reduction of CO$_2$. AcN, as aprotic organic solvents with very low viscosity, was often used in the electrochemical reaction process [1, 7]. Therefore, ILs/AcN mixtures were used in the study as electrolyte. When the [N$_{1118}$][TRIZ]/AcN were saturated with N$_2$ and CO$_2$ respectively, features changed in the CV responses occurred, as shown in Fig. 2. The significant measurements difference in the N$_2$-saturated and CO$_2$-saturated environment concerned the onset potential and the current density, indicating that the reduction of CO$_2$ occurs on the Ag electrode. Meanwhile, the content ILs [N$_{1118}$][TRIZ] effected onset potential and the current density. It is worth to mention that the potential causing a current density of 0.6 mA cm$^{-2}$ was chosen as the onset potential of CO$_2$ reduction following the study of Lu et al. [21]. Therefore, the same onset potentials (-1.93 V (vs. Ag/Ag$^+$)) were found in different content of [N$_{1118}$][TRIZ] saturated with CO$_2$ (Fig. 2), while the cathodic current density increased exponentially with [N$_{1118}$][TRIZ] content increased from 10 wt% to 50 wt% at potentials < -1.93 V(vs. Ag/Ag$^+$). The current density tended to increase first and then decreased, and the highest current density for CO$_2$ reduction was obtained at the [N$_{1118}$][TRIZ] content of 20 wt%. The main reason was that the ILs acted as a supporting electrolyte, resulting in different conductivity.
Fig. 3. (A) The effect of [N\textsubscript{1118}][TRIZ] content on the current density and Faradaic efficiency with Ag electrode at -2.3 V (vs. Ag/Ag\textsuperscript{+}); (B) The effect of applied potential on Ag cathode in [N\textsubscript{1118}][TRIZ](20 wt%)/AcN electrolyte at -2.3 V (vs. Ag/Ag\textsuperscript{+}).

The effect of [N\textsubscript{1118}][TRIZ]-containing in binary electrolytes [N\textsubscript{1118}][TRIZ]/AcN on the electrocatalytic activity of CO\textsubscript{2} reduction and the product selectivity were explored with Ag electrodes at -2.3 V (vs. Ag/Ag\textsuperscript{+}) for 2 h, as illustrated in Fig. 3(A). As demonstrated in Fig. 3(A), over 10 wt% [N\textsubscript{1118}][TRIZ] content, the CO efficiency never fell below 90%. Clearly, the predominant CO formation prevented the formation of by-products H\textsubscript{2} in the [N\textsubscript{1118}][TRIZ] electrolyte. When the [N\textsubscript{1118}][TRIZ] contents were more than 20 wt%, the current density decreased. The reason was that electrostatic attraction between the cation and anion of ILs, causing the movement of ions to be blocked and the decrease of charge transfer rate. Remarkably, the current density was up to 50.8 mA/cm\textsuperscript{2} with a Faradaic efficiency of 90.6% at -2.3 V (vs. Ag/Ag\textsuperscript{+}) in [N\textsubscript{1118}][TRIZ](20 wt%)/AcN electrolyte. As mentioned previously, the current density obtained by using the [N\textsubscript{1118}][TRIZ](20 wt%)/AcN electrolyte was much higher than those reported in the ILs electrolyte (Fig. 3(A); Supporting Information, Table S1). These results showed that the binary [N\textsubscript{1118}][TRIZ]/AcN mixtures yielded high total current densities and high CO selectivities. The corresponding potential dependent in the [N\textsubscript{1118}][TRIZ](20 wt%)/AcN was conducted using Ag as electrode, as shown in Fig. 3(B). The data showed that the Faraday efficiency
exceeded 90% when the applied potentials were -2.2 V (vs. Ag/Ag+) and -2.3 V (vs. Ag/Ag+) respectively.

Water as important proton source provided the protons needed for CO2 electrocatalytic reduction. A small amount of H2O in the process of electrocatalytic CO2 reduction is beneficial to the reduction of CO2 [7, 22]. Hence, the effect of water on electrocatalytic CO2 reduction was investigated (Fig. 4). Herein, the water content was calculated based on AcN. Fig. 4(A) showed the CVs for the reduction of CO2 on [N1118][TRIZ](20 wt%)/AcN-H2O electrolyte. As the addition of water, it could be observed that the onset potential for the CO2 reduction gradually moved to more positive potentials relative to the CO2-saturated [N1118][TRIZ]/AcN electrolyte (Fig. 3(A)). The onset potential of CO2 reduction increased from -1.93 V to -1.75 V vs. Ag/Ag+, as the water content increased from 0 wt% to 7.5 wt%. Lowering the initial reduction energy barrier upon water addition may be explained by increased the availability of proton near Ag electrode surface, which was beneficial to the CO2 reduction [11]. Fig. 4(B) exhibited that the current density increased sharply with up to 7.5 wt% H2O content. However, the selectivity of CO decreased obviously (Fig. 4(B)), and it increased significantly for H2, indicating that addition of too much water was to the disadvantage of CO2 reduction. At the same time, Faraday efficiency of 86.2% with the 5 wt% H2O was obtained, and the current density of 61.7 mA cm−2 was slightly lower than the current density at the water content of 7.5 wt%. The above analysis results showed that the high water content started to dominate the product distribution. This is consistent with literature [11, 14]. Considering better current density and Faraday efficiency with a water content of 5 wt%, we further explored the effect of applied potential in the [N1118][TRIZ](20 wt%)/AcN-H2O(5 wt%) mixtures.
Fig. 4. The effect of adding H₂O to [N₁₁₁₈][TRIZ](20 wt%)/AcN on CO₂ reduction on Ag cathode. (A) CVs measurements; (B) H₂O amount; (C) The effect of applied potential on Ag cathode in [N₁₁₁₈][TRIZ](20 wt%)/AcN-H₂O(5 wt%) electrolyte at -2.3 V (vs. Ag/Ag⁺); (D) Partial current density of CO in different applied potential.

The effect of applied potential in the [N₁₁₁₈][TRIZ](20 wt%)/AcN-H₂O(5 wt%) mixtures illustrated in Fig. 4(C). Obviously, the total current density and CO partial current density (Fig. 4(D)) increased with the increased of applied potential. At medium applied potentials ranged from -2.0 V to -2.1 V (vs. Ag/Ag⁺), the CO efficiency higher than 91%. At -2.0 V (vs. Ag/Ag⁺), the Faraday efficiency of CO achieved a maximum value of 92.2% with a current density of 21.2 mAcm⁻². The above results indicated that the ILs helped to provide a low energy with high current density and Faraday efficiency for CO₂ electroreduction.

3.2. DFT Calculations
Fig. 5. The lowest energy configurations: (A) CO$_2$; (B) [N$_{1118}$][TRIZ]-CO$_2$. N atom (blue), C atom (gray), H atom (white). (C) Energy level diagram of CO$_2$ molecular orbital; (D) Energy level diagram of after CO$_2$ activation.

Table 1
Van Der Waals radius rw (nm) of atoms [23]

|     | C   | H   | Br  | Cl  | N   | O   | P   | S   |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|     | 1.72| 1.2 | 1.85| 1.75| 1.55| 1.5 | 1.8 | 1.8 |

Table 2
DFT calculation results of CO$_2$ and [N$_{1118}$][TRIZ]-CO$_2$

|                        | C=O bend length (Å) | Bond angle (°) |
|------------------------|---------------------|----------------|
| CO$_2$ (Fig. 5(A))     | 1.16 (2O---1C)     | 180            |
|                        | 1.16 (3O---1C)     |                |
| [N$_{1118}$][TRIZ]-CO$_2$ (Fig. 5(B)) | 1.24 (40O---39C) | 130.2          |
|                        | 1.25 (41O---39C)   |                |

The quantum chemical calculations were carried out to explore the underlying mechanism of [N$_{1118}$][TRIZ] activating CO$_2$. As was evident in Fig. 5(B), the most stable configuration between [N$_{1118}$][TRIZ] and CO$_2$ was obtained by structure optimization. The foremost feature of hydrogen bond
was that the proton–acceptor distance was shorter than the corresponding sum of their van der Waals radii [23] (Table 1). The calculation result in Fig. 5(B) showed that the interatomic distances of 40O⋯16H (2.05 Å), 41O⋯4H (2.13 Å), and 41O⋯11H (2.11 Å) represented strong hydrogen bond interactions, including that the cation formed hydrogen bonds with CO₂. Furthermore, the hydrogen bonding strength of 40O⋯16H (2.05 Å) compared with those 41O⋯4H (2.13 Å) and 41O⋯11H (2.11 Å) was much stronger (Table 2). Moreover, N atom at the 4-position (45N) of 1,2,4-triazole preferred to coordinate with C atom of CO₂ because of its strong electronegativity, resulting in a formation of [TRIZ-CO₂]- complex.

Table 3

NPA charge of CO₂ and NPA charge of CO₂ in [N₁₁₁₈]⁺[TRIZ-CO₂]- complex

| CO₂         | Net charge | [N₁₁₁₈]⁺[TRIZ-CO₂] | Net charge |
|-------------|------------|--------------------|------------|
| Atom        |            | Atom               |            |
| C           | 0.99041    | C(39)              | 0.46314    |
| O           | -0.49520   | O(40)              | -0.37486   |
| O           | -0.49520   | O(41)              | -0.39492   |
| Total charge| 0.00000    | Total charge       | -0.30664   |

The Natural Bond Orbital (NBO) analysis was performed, aiming at getting more detailed information of CO₂ activation process (Fig. 5(C), Fig. 5(D) and Table 3). Based on molecular orbital theory, the CO₂ molecular bonding orbital consisted of the double electrons occupied orbitals (σ and π) and the electron unoccupied antibonding orbitals (σ* and π*) (Fig. 5(C)), as such the CO₂ molecule was relatively stable. Particularly, according to Natural Population analysis (NPA) in the [N₁₁₁₈]⁺[TRIZ-CO₂]- complex, the net charge of CO₂ is -0.307 e compared to the isolated neutral CO₂ molecule (Table 3), which showed that CO₂ got electrons from [TRIZ] anion. The additional electron of CO₂ was filled in the Lowest Unoccupied Molecular Orbital (LUMO), which was mainly composed of the anti-bonding orbit of CO₂. Hence, that is to say, the obtained electron of CO₂ from [TRIZ] preferred to occupy the anti-bonding orbit (π*) (Fig. 5(D)), thus reducing the electron density between C and O in CO₂. On the basis of molecular orbit theory, the higher π* occupancy or σ* occupancy, the higher energy of the system, thus weakening the chemical bond and reducing the bond energy [24].
Therefore, C=O bond energy could be weakened owing to the introduction of anti-bonding orbit electrons. This is also the reason why the C=O changed from 1.16 Å to 1.24 Å and 1.25 Å (Table 2). It could be seen from Fig. 5(B) that the linear spatial distribution of CO₂ molecule (C, sp hybridization) altered to the bent configuration (C, near sp² hybridization) with O-C-O bond angle of 130.2° after the action of [N₁₁₁₈][TRIZ]. At the same time, the CO₂ molecule was lengthened asymmetrically from the original symmetric C=O, as shown in Table 2. The above analysis demonstrates that [N₁₁₁₈][TRIZ] is able to provide a low energy path for CO₂ electrocatalytic reduction.

3.3. Catalytic mechanism

![Fig. 6. Possible mechanism of electrochemical reduction of CO₂ to CO on Ag cathode in [N₁₁₁₈][TRIZ]-containing catholytes.](image)

The mechanism of electrocatalytic reduction of CO₂ to CO in imidazole based ILs electrolyte had been studied by many researches [6, 11]. Imidazole cations play a key role in this kind of electrolyte. However, unlike conventional imidazole-based ILs, the [N₁₁₁₈][TRIZ] mainly affects the reaction process by anion. Hence, a mechanism different from imidazolium-based ILs was proposed for the
electrocatalytic CO\textsubscript{2} reduction to CO on Ag cathode in [N\textsubscript{1118}][TRIZ]-containing catholytes (Fig. 6) based on the experimental studies in the open literature [25-27]. From Section 3.2, the CO\textsubscript{2} molecule receives extra electron from the [TRIZ]\textsuperscript{-}, leading to more higher \(\pi^*\) occupancy, which caused CO\textsubscript{2} to change from linear to bend. Formation of [N\textsubscript{1118}]\textsuperscript{+}[TRIZ-CO\textsubscript{2}]\textsuperscript{-} complex could lower the reaction energy barrier of CO\textsubscript{2} reduction. Subsequently, the [N\textsubscript{1118}]\textsuperscript{+}[TRIZ-CO\textsubscript{2}]\textsuperscript{-} complex was adsorbed on the surface of the Ag electrode and formed [N\textsubscript{1118}]\textsuperscript{+}[TRIZ-CO\textsubscript{2}]\textsuperscript{-} layer. The surface of Ag electrode was enriched with electrons under the effect of applied potential, and an electron from Ag surface tended to transfer to the anti-bonding orbital (\(\pi^*\)) of the activated CO\textsubscript{2} by [N\textsubscript{1118}][TRIZ]. As a result, the bent CO\textsubscript{2} got an electron from the donor to form an adsorbed CO\textsubscript{2}\textsuperscript{-} radical on the surface of Ag. After that, CO\textsubscript{2}\textsuperscript{-} radical combined with a CO\textsubscript{2} to generate adduct of (CO\textsubscript{2})\textsubscript{2}\textsuperscript{-}. Finally, (CO\textsubscript{2})\textsubscript{2}\textsuperscript{-} formed CO by obtaining an electron. The product CO diffused into bulk solution through the gap between the adsorption ILs layers.

4. Conclusion

In this work, we presented a new ILs [N\textsubscript{1118}][TRIZ] for electrocatalytic CO\textsubscript{2} reduction on a commercial Ag electrode. The result demonstrated that the [N\textsubscript{1118}][TRIZ]/AcN system exhibits excellent performance for CO\textsubscript{2} electroreduction to CO with current density of up to 50.8 mAcm\textsuperscript{-2} and a CO Faradaic efficiency of 90.6%. The [N\textsubscript{1118}][TRIZ] (20 wt%)/AcN-H\textsubscript{2}O (5 wt%) mixture electrolyte showed that the Faradaic efficiency of 92.2% with a current density of 21.2 mAcm\textsuperscript{-2} could be obtained. These excellent effects came from the activation of CO\textsubscript{2} by [N\textsubscript{1118}][TRIZ]. According to NBO analysis, the electrons obtained from [N\textsubscript{1118}][TRIZ] would be filled in the anti-bonding orbit (\(\pi^*\)) of the CO\textsubscript{2}, thus reducing the reduction barrier required for electrocatalytic CO\textsubscript{2} reduction. From the achievements in this contribution, we believe that it is possible to conduct a commercial process for electrochemical CO\textsubscript{2} reduction with the help of the new ILs-based electrolyte in combination with non-precious metal catalysts.
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Appendix A. Supplementary data

Supplementary material related to this article can be found in the online version.

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