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Accepted Article

Title: Novel Aromatic Ester-Functionalized Ionic Liquid for Highly Efficient CO2 Electrochemical Reduction to Oxalic Acid

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.202001194

Link to VoR: https://doi.org/10.1002/cssc.202001194

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Novel Aromatic Ester-Functionalized Ionic Liquid for Highly Efficient CO₂ Electrochemical Reduction to Oxalic Acid

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Abstract: Electrochemical reduction of CO₂ into valuable chemicals is a significant route to utilize CO₂ resources. Among various electroreduction products, oxalic acid (H₂C₂O₄) is an important chemical for pharmaceutical, rare earth extraction and metal processing. Here, we designed a novel aprotic aromatic esterfunctionalized ionic liquid (IL) of [TEA][4-MF-PhO] as an electrolyte for CO₂ electroreduction into oxalic acid. It exhibited a large oxalic acid partial current density of 9.03 mA cm⁻² with a Faradaic efficiency (FE) of 86 % at -2.6 V (vs. Ag/Ag⁺), and the oxalic acid formation rate is as high as 168.4 μ mol cm⁻² h⁻¹, which is the highest reported value to date. Moreover, the results with density functional theory (DFT) calculations demonstrated that CO₂ was efficiently activated to -COOH intermediate by bis-active sites of the aromatic ester anion via the formation of [4-MF-PhO - COOH]⁻ adduct, which finally dimerized into oxalic acid.

The unprecedented emissions of carbon dioxide (CO₂) has led to an undesirable impact on global climate and environment.^[1] However, with regards to CO₂ as a natural, abundant and inexpensive C1 feedstock,^[2] the conversion of CO₂ to high value-added chemicals is benefit both for environment and economy.^[3] with reduction^[4] Compared thermal and photocatalytic reduction,^[5] electrochemical reduction^[6] is a promising method because of simple operation and easy industrial amplification under mild conditions.^[7] Among various CO2 electrochemical reduction products, oxalic acid is an important chemical widely used in pharmaceutical, rare earth extraction, metal processing and so on.^[8] The traditional oxalic acid production processes include sodium formate method, coupling gas phase method from CO and polysaccharide oxidation method,^[9] which suffer from the problems of high raw material cost, low yield, and serious pollution, etc.^[10] Therefore, the development of high efficient electrochemical CO_2 reduction system for oxalic acid is of great significance.

Previous studies about CO₂ electroreduction to oxalic acid were focused on the introduction of ordinary quaternary ammonium salts auxiliary electrolyte^[11] and the development of metal complexes catalysts^[12], which improved the Faradaic efficiency (FE) of oxalic acid to more than 90 %, but the partial current density (< 6 mA cm⁻²) and formation rate of oxalic acid (< 120 μ mol cm⁻² h⁻¹) are very low. The reaction process of CO₂ electroreduction to oxalic acid generally involves the reduction of CO_2 to CO_2 . radical anion intermediate and the dimerization process for CO2.- into C2O42-[13] When the electrolyte contains active proton H, the CO2.- intermediate easily combines with H to form formic acid preferentially,[14] so aprotic electrolytic environment is important to produce oxalic acid.^[15] Gennaro et al.^[16] added the aromatic ester or aromatic nitrile compound into 0.1 M n-Bu₄NClO₄-DMF aprotic electrolyte solution, resulting in higher FE of oxalate product as 99 %. However, the current density was only 1.6 mA cm⁻², and the oxalate formation rate was less than 30 µmol cm⁻² h⁻¹.

As a new type of medium composed entirely of anion and cation, ionic liquids (ILs) are used in CO₂ electroreduction as an excellent electrolyte because of the unique properties for high efficient CO₂ dissolution and activation, precise control products, and high conductivity, etc.^[17] At present, there were almost no any reports of CO₂ electroreduction to oxalic acid in IL electrolyte systems. Inspired by these reports^[15, 16, 18], we designed an aprotic aromatic ester-functionalized IL for CO₂ electroreduction to oxalic acid in order to achieve high current density and FE by enhancing CO₂ dissolution and activation under the effect of IL with bis-active sites.

Herein, we conducted firstly CO_2 electrochemical reduction to oxalic acid using a novel aromatic ester anion functionalized IL of 4-(methoxycarbonyl) phenol tetraethylammonium ([TEA][4-

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MF-PhO]). The principle of designing [TEA][4-MF-PhO] is based on the catalysis of aromatic esters and the stability of the quaternary ammonium salt in electrolyte solution. More importantly, the increase of multiple active sites with phenol and ester groups in IL could cause the large current density. In addition to the design the structure of the IL, screening a suitable electrolyte system is also a nodus. The combination of [TEA][4-MF-PhO] and aprotic acetonitrile solvent not only effectively improves the CO2 mass transfer rate, but also provides aprotic electroreduction environment for CO₂, which is conducive to the generation of oxalic acid. Our results showed that the partial current density reached 9.03 mA cm⁻² with an oxalic acid formation rate of 168.4 µmol cm⁻² h⁻¹, which is the highest value in the literature to date. To investigate the interaction between [4-MF-PhO]⁻ and CO₂, density functional theory (DFT) calculations were performed. Subsequently, a possible reaction mechanism was proposed.

[TEA][4-MF-PhO] was synthesized by tetraethylammonium hydroxide and methyl 4-hydroxybenzoate via one-step reaction. The structure of [TEA][4-MF-PhO] was shown in Figure 1, and the result of nuclear magnetic resonance (NMR) confirmed [TEA][4-MF-PhO] was synthesized successfully (Figure S1). The viscosity is fundamental physical parameters of ILs. Since the electrolyte system is a mixture of IL and acetonitrile (AcN, aprotic solvent), the viscosities of [TEA][4-MF-PhO] and [TEA][4-MF-PhOl-AcN solution with different IL mass fractions were tested. Figure S2 shows that viscosities of various mass fraction IL decrease with increasing temperature, and the viscosity of pure IL is greatly affected by temperature. In addition, as the mass fraction of IL decreasing from 100 wt% to 30 wt%, the viscosity decreases from 1406.7 to 0.5 mPa s. The lower viscosity of electrolyte is beneficial to mass transfer in the reaction process, so we adopt a mixture system with IL-AcN for the electrolysis experiment. The CO2 absorption experimental was conducted by the apparatus represented in Figure S3, and the CO₂ absorption capacity in [TEA][4-MF-PhO] was plotted in Figure S4. 0.58 mol CO₂ per mol IL was obtained at 323.15 K under ambient pressure. Adequate CO2 in the electrolyte can effectively facilitate the electrochemical conversion of CO2 according to previous reports.[3a]



Figure 1. Molecular structures of (a) [TEA][4-MF-PhO], (b) [TEA][BF₄], (c) [TEA][PF₆] and (d) [Bmim][BF₄].

The electrochemical experiments were carried out with the Htype cell^[2] and using Pb as working electrode (Figure S5). As revealed by LSV results (Figure 2a), the system with N₂saturated electrolyte exhibited much lower current density than that with CO₂-saturated electrolyte, which testifying the occurrence of CO₂ electroreduction. The current density as a function of time at different potentials (vs. Ag/Ag⁺, all potentials in this paper are vs. Ag/Ag⁺) of -2.5 V to -2.9 V in the [TEA][4-MF-PhO] (0.9 M)-AcN mixture were shown in Figure 2b. The i-t curves show that the current density is stable in the overall reaction time of 2 h, indicating that the [TEA][4-MF-PhO] exhibits a good stability.



Figure 2. The CO₂ electrochemical reduction performance at Pb electrode. (a) The LSV curves in N₂ and CO₂ saturated electrolytes and (b) the i-t curves in [TEA][4-MF-PhO] (0.9 M)-AcN electrolyte.

The potentiostatic electrolysis experiments were performed to investigate the products distribution of CO2 electroreduction in [TEA][4-MF-PhO] system, and [TEA][BF₄], [TEA][PF₆] and [Bmim][BF₄] were also tested for comparison. Due to the low solubility of [TEA][PF₆] in AcN, 0.1 M [TEA][PF₆]-AcN electrolyte was selected. After 2 h potentiostatic electrolysis, the partial current density and FE for oxalic acid in various ILs-AcN electrolytes were measured. As shown in Figure 3a and Figure 3b, [TEA][4-MF-PhO] (0.9 M)-AcN exhibits an excellent catalytic activity. For instance, the highest FE of 86 % with partial current density for H₂C₂O₄ (9.03 mA cm⁻²) at -2.6 V are obtained, and the relatively high oxalic acid FE (>70%) can be kept in a wide range of potentials (-2.5 ~ -2.8 V). However, the FE for oxalic acid in [TEA][BF₄], [TEA][PF₆] and [Bmim][BF₄] electrolyte systems are less than 35% entirely, which are much lower than that of [TEA][4-MF-PhO].



Figure 3. The effect of various ILs on the CO₂ electroreduction to oxalic acid. (a) FE and (b) partial current density of oxalic acid at applied potential of -2.5 V to -2.9 V (vs. Ag/Ag⁺) in various ILs-AcN electrolytes.

In particular, various electrolysis products and FE at a controlled potential of -2.6 V in different ILs-AcN system was exhibited in Figure 4, which were quantified based on the

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standard curves of oxalic acid, formic acid, CO and H₂ (Figure S6). It is clear that the FE for oxalic acid followed the order of [TEA][4-MF-PhO]>[TEA][BF₄]>[TEA][PF₆]>[Bmim][BF₄]. Typically, there was no oxalic acid generated in [Bmim][BF₄] electrolyte, and most of CO₂ was converted to HCOOH. According to the performance of [TEA][4-MF-PhO], [TEA][BF₄] and [TEA][PF₆], it was found that anions play a significant role in the reaction of CO_2 electroreduction to $H_2C_2O_4$. The reason is probably attributed to the difference of the interaction between CO2 and the anions of the ILs. On the other hand, a large amount of HCOOH is obtained instead of H2C2O4 in [Bmim][BF4]-AcN system, which is attributed to the active proton H exist on the imidazole, and it easily combines with the activated CO2.- to form HCOOH. However, [TEA]⁺ provides an aprotic electroreduction environment for CO₂, which is more conducive to generating oxalic acid. Moreover, large current density and high FE of oxalic acid result in the remarkable oxalic acid formation rate.^[19] The oxalic acid formation rate in [TEA][4-MF-PhO] reaches as high as 168 µmol cm⁻² h⁻¹ at the optimal potential, which is the highest value among the reported values of CO₂ electroreduction to oxalic acid up to now (Figure 5).



Figure 4. FE of electrolysis products for $H_2C_2O_4,$ HCOOH, CO and H_2 in various ILs-AcN electrolytes at -2.6 V (vs. Ag/Ag*) on Pb electrode.



Figure 5. Comparison of oxalic acid partial current density and formation rate in [TEA][4-MF-PhO]-AcN electrolyte at Pb electrode with other electrolytes and electrodes system in literature.

The effect of [TEA][4-MF-PhO] content in the IL-AcN electrolyte on CO₂ electroreduction performance was investigated, and the LSV curves at different [TEA][4-MF-PhO] contents were shown in Figure S7a. The current density increases and the onset potential decreases as the IL content increase (from 0.6 to 0.9 M). The potentiostatic electrolysis were performed at -2.6 V to investigate the influence of IL content on oxalic acid partial current density and FE. As shown in Figure S7b, the partial current density and FE of oxalic acid significantly increase until IL content is up to 0.9 M. The phenomenon could be explained that the number of ions increase with the IL content increase, resulting in an increasing conductivity of the electrolyte. Nevertheless, the oxalic acid partial current density and FE decrease distinctly above 0.9 M IL. This attributed to the reason that the electrostatic attraction between the IL cations and anions is enhanced and hindering the movement of the ionic species. Therefore, 0.9 M [TEA][4-MF-PhO] content is suitable

for CO₂ electroreduction to oxalic acid. The influence of H₂O content in the electrolyte solution was also investigated. The LSV curves in IL (0.9 M)-AcN-H₂O electrolyte with various H₂O content (1.0 wt%, 2.5 wt%, 5.0 wt%) and 10.0 wt%) were shown in Figure S8. It shows that the onset potential decreases with the increase of H₂O content in ternary electrolyte. Furthermore, Figure S9 exhibits the partial current density of H₂C₂O₄ and FE of all reduction products in IL-AcN-H₂O electrolyte with different H₂O content at -2.6 V. The FE and partial current density of oxalic acid drop sharply with the increase of H₂O content from 0 to 10.0 wt%. Under anhydrous condition, the highest FE for oxalic acid with 86 % is obtained, and the by-products are mainly CO with a bit of H₂. When H₂O content exceeds 10.0 wt%, oxalic acid is hardly produced. The reason is that the presence of water in the electrolyte provides proton H and breaks the aprotic electroreduction environment, which easily combines with the activated CO₂.⁻ to form HCOOH. Comprehensively speaking, the addition of water to electrolyte is capable of increasing reduction current and lowing onset potential, but reducing the selectivity to H₂C₂O₄ and inhibiting the yield of H₂C₂O₄. That is, the FE of oxalic acid can be easily controlled by adjusting H₂O content in the catholyte.

In order to evaluate the interaction between aromatic ester anion of [4-MF-PhO]⁻ and CO₂, DFT calculations were performed. Figure S10a and Figure S10b illustrate that the [4-MF-PhO]⁻ with phenoxy and ester double active sites can effectively bend a stable linear CO₂ molecule to CO₂-⁻ with O-C-O bond angle of 140° and 145° respectively, which is consistent with previous reported.^[16, 20] After that, Figure S10c and Figure S10d show the activated [4-MF-PhO]-CO₂-⁻ combines with H⁺ provided by anodic electrolyte to form the [4-MF-PhO - COOH]⁻. Importantly, the O-C-O bond angle of -COOH intermediate with 126° is close to oxalic acid (125°). The DFT calculations indicate that the aromatic ester IL of [TEA][4-MF-PhO] is indeed beneficial to CO₂ electroreduction to oxalic acid.

For CO₂ electroreduction into oxalic acid, Gennaro et al.^[16] indicated that the catalytic effect of esters on CO₂ is conducive to the formation of CO₂ anion radical. On the basis of the above viewpoint, and the results of further study on the O-C-O bond angle, we proposed a possible mechanism as shown in Figure 6. During the electroreduction process, CO₂ is activated by [4-MF-PhO]⁻ to form a new C-O single bond with the O atom, and the [4-MF-PhO]-CO₂-⁻ is easily combined with H⁺ to generate [4-MF-PhO] - COOH]⁻ adduct at the same time. The C-O bond newly

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formed is successively broken, generating the parent aromatic ester IL of [TEA][4-MF-PhO] and -COOH intermediate, which eventually dimerize to oxalic acid.



Figure 6. Mechanism of CO_2 electroreduction to oxalic acid on Pb electrode in the [TEA][4-MF-PhO] (0.9 M)-AcN electrolyte.

In summary, we have designed and applied a novel aromatic ester-functionalized IL to enhance the CO_2 electrochemical reduction into oxalic acid for the first time. It was found that the exceptionally high partial current density (9.03 mA cm⁻²) for oxalic acid with appreciable FE (86 %) on Pb electrode were reached in anhydrous [TEA][4-MF-PhO] (0.9 M)-AcN cathodic electrolyte, which is much higher than other reported values to date. Furthermore, the formation rate of oxalic acid is as high as 168.4 µmol cm⁻² h⁻¹. Subsequently, a related mechanism was proposed, which reveals the unique role of IL, especially the aromatic ester anion with bis-active sites on the CO_2 dissolution, activation, and selectivity conversion to oxalic acid. This work proved that aprotic IL with active site can enhance the efficiency of CO_2 electroreduction to oxalic acid significantly, and open up a potential path for the production of oxalic acid with CO_2 .

Experimental Section

Materials

Gases used in absorption and electrochemical experiments including CO₂, CO, N₂, and H₂ were purchased from Beijing Beiwen Gas Factory. Acetonitrile (HPLC Grade) and ethanol (C₂H₅OH, AR, ≥99.7%) were purchased from Fisher Chemical and Tianjin Damao Chemical Reagent Factory, respectively. Oxalic acid Standard was obtained from Dr. Ehrenstorfer GmbH. Silver perchlorate (anhydrous) was purchased from Alfa Aesar Chemical Co., Ltd. Tetrabutylammonium perchlorate (for electrochemical analysis, ≥99.0%) was obtained from Sigma-Aldrich. AR reagents including Tetraethylammonium hydroxide, Methyl 4-hydroxybenzoate, Tetraethylammonium tetrafluoroborate, Tetraethylammonium hexafluorophosphate, and 1-Butyl-3-methylimidazolium tetrafluoroborate were purchased from Aladdin Biochemical Technology Co., Ltd. Potassium phosphate monobasic (for HPLC, ≥99.5%) and Phosphoric acid (for HPLC) were obtained from Macklin Biochemical Technology Co., Ltd.

Synthesis and characterization of ionic liquid.

[TEA][4-MF-PhO] is synthesized by a one-step method of a neutralization reaction. A certain amount of methyl 4hydroxybenzoate is dissolved into 50 mL ethanol in a 250 mL single round-bottom flask under magnetic stirring. An equimolar amount of tetraethylammonium hydroxide aqueous solution is added dropwise into the flask using a constant pressure funnel. The mixture is kept stirring at 303.15 K for 12 h to allow complete reaction. Subsequently, ethanol and water are removed via rotary evaporation at 333.15 K and 348.15K under reduced pressure, respectively. At last, the IL obtained is dried in a vacuum oven at 333.15 K for 48 h to eliminate trace water and organic solvent. The water content in the ILs is determined by means of Mettler Toledo Coulometric KF titrator C20 detection (Karl Fischer titration). In this work, the water content in ILs is less than 100 ppm. The molecular structure of [TEA][4-MF-PhO] is confirmed by ¹H NMR and ¹³C NMR spectra. (Supporting Information, Figure S1). The viscosities of the IL and IL-AcN complex solution are measured by an Anton Paar Lovis 2000 M/ME viscometer with a temperature range from 293.15 K to 343.15 K, at intervals of 10 K (Supporting Information, Figure S2).

CO₂ absorption experiment

The CO₂ absorption experimental setup was schematically represented in Figure S3 (Supporting Information), and the procedures was based on our previous work.^[1] Typically, the CO₂ absorption experiment in IL was implemented at the temperature of 323.15 K and atmospheric pressure. CO₂ gas is bubbled into the IL (about 5 g) through a glass container with an inner diameter of 2 cm. The flow rate of CO₂ is about 200 ml min⁻¹, and the glass container is partially immersed in a water bath to ensure the system temperature. The amount of CO₂ absorbed in the IL is determined at intervals by an electronic balance with an accuracy of ±0.1 mg.

Electrochemical Test

Electrochemical measurements were performed using a commonly used H-type cell at ambient temperature and pressure. The anode and cathode compartments are separated by Alfa Nafion 117 proton exchange membrane. The volume of the anode chamber and cathode chamber are both 40 mL with a 30 mm diameter of each chamber. In a typical electrochemical reduction, IL-AcN solution and 0.1 M H₂SO₄ aqueous solution are served as cathodic and anodic electrolytes, respectively. The amount of electrolyte used is 27 mL in all the experiments. Prior to the beginning of measurement, the catholyte is bubbled with CO₂ at a gas flow rate of 30 mL min⁻¹ for 30 min under magnetic stirring to insure the solution was saturated with CO₂, a N₂-saturated solution is also used for comparison. In the reaction process, an electrochemical workstation (CHI 660E, Shanghai CH Instruments Co., China) was applied to monitor the potential of the experiments. Linear Sweep Voltammetry (LSV) measurements were recorded to determine the appropriate potentials for the reduction with three-electrode configuration. The working electrode is a lead sheet with a 1 cm² surface area, which is polished by #1000 sandpaper and then is sonicated in ethanol and acetone for 5 minutes, followed by rinsing with acetonitrile, and finally dried in N₂ atmosphere before each set of experiment. The reference electrode is 0.01 M Ag/Ag⁺ constituted by dissolving 0.01 M AgCIO₄ in 0.1 M TBAP-AcN and segregates from the catholyte by a glass casing. The counter electrode is a 1 x 1 cm platinum gauze (Pt, purity >99.99%). LSV tests are recorded from -2.1 V to -3.0 V (vs. Ag/Ag⁺) at a scan rate of 50 mV s⁻¹ in gas-saturated electrolyte. Afterward, the potentiostat electrolysis were performed at controlled

potentials with light magnetic stirring during the process for better mixing. After a desired electrolysis time, the gaseous product and cathodic electrolyte were collected up for analysis, respectively.

Products analysis

 $H_2C_2O_4$ and HCOOH were the liquid products quantified by highperformance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR) spectroscopy. CO and H_2 were the gaseous products according to the analysis of chromatography (GC) data. The gaseous products after electrochemical reduction of CO₂ were analyzed by gas chromatography (GC, Agilent 7890B) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Separation of CO, H_2 and CO₂ is performed on a double column system with an analytical column of molecular sieve 5A and haye Sep Q column. During the detection, High purity nitrogen is used as a carrier gas. The H_2 is detected and determined directly when the gas stream passs through the TCD detector, and the CO is quantitatively measured when the gas stream passes through the FID detector.

The liquid phase products were mainly analyzed by ¹H NMR spectroscopy and high-performance liquid chromatography (HPLC). The electrolyte sample is dissolved in deuterated dimethyl sulfoxide (d₆-DMSO) solvent with phenol as an internal standard, and the formic acid product is determined and quantified by using a 600 MHz liquid NMR spectrometer. On the other hand, the amount of oxalic acid product is detected by HPLC, performed on Shimadzu LC-20AT HPLC instrument equipped with a UV detector using an InertSustain AQ-C18 reverse column (5 μ m, 4.6 × 250 mm). The mobile phases are acetonitrile and 20 mM KH₂PO₄ aqueous solution with a PH of 2.5, the flow ratio is 5: 95 at a total flow rate of 0.5 mL min⁻¹.

The quantum chemical calculations

In order to confirm the effect of [TEA][4-MF-PhO], especially the functional aromatic ester anion of [4-MF-PhO]⁻ on the CO₂ activation and the selective regulation of oxalic acid products, quantum chemical calculations were carried out. The gaussian calculation was performed to evaluate interaction between anion and CO₂, the structural optimizations of [4-MF-PhO-CO₂] were implemented at the B3LYP/6-31++G (d, p) theoretical level by density functional theory (DFT) calculations. Furthermore, considering the role of the Pb electrode, Vienna ab-initio Simulation Program Package (VASP) calculation was used to optimize the structure of CO₂ under the action of [4-MF-PhO]⁻ and Pb electrode system.

Acknowledgements

This work is financially supported by the National Key R&D Program of China (2018YFB0605802), the National Natural Science Foundation of China (21838010, 51574215), the Major Program of National Natural Science Foundation of China (21890760, 21890762), the program of Beijing Municipal Natural Science Foundation (2182072, 2182071), the DNL Cooperation Fund, CAS (DNL 180406), and the Zhengzhou High Level Talent (No. 20180200029).

Keywords: aromatic ester-functionalized ionic liquid • CO₂ reduction • electrocatalyst • electrolysis conversion • oxalic acid

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A novel aprotic aromatic ester-functionalized IL of [TEA][4-MF-PhO] was designed for CO2 electroreduction to oxalic acid. The multiple active sites exhibit excellent catalytic performance of high current density and Faradaic efficiency for oxalic acid via interacting with CO₂. This study provides a promising prospect for using IL as electrolyte to develop efficient electrocatalysts.