

Computational studies of ionic liquids as co-catalyst for CO₂ electrochemical reduction to produce syngas using COSMO-RS

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Abstract. Transforming carbon dioxide (CO₂) into value-added products through electrochemical reduction reaction (CO₂ERR) is a promising technique due to its potential advantages using renewable energy. The main challenge is to find a stable catalytic system that could minimize the reaction overpotential with high faradaic efficiency and high current density. Ionic liquids (ILs) as electrolyte in CO₂ERR have attracted attention due to the advantages of their unique properties in enhancing catalytic efficiency. For better performance, a systematic understanding of the role of ILs as electrocatalyst is needed. Therefore, this paper aims to correlate the performance of ILs as co-catalyst in (CO₂ERR) with the lowest unoccupied molecular orbital (LUMO) energy level and the interaction energy as predicted by quantum chemical calculation using Conductor like Screening Model for Real Solvents (COSMO-RS) and Turbomole. The results show strong linearity ($R^2=0.98$) between hydrogen bond energy (HB) and LUMO values. It is demonstrated that as HB increases, the LUMO value decreases, and the catalytic activity for CO₂ERR also increases. This result allows further understanding on the correlation between the molecular structure and the catalytic activity for CO₂ERR. It can serve as a priori prediction to aid in the design of new effective catalysts.

Keywords: Ionic liquid, CO₂ electrochemical reduction, COSMO-RS

1 Introduction

Greenhouse gasses, particularly carbon dioxide, are rapidly increasing as a result of the unregulated use of fossil fuels, which has led to severe environmental problems in recent years. Though CO₂ is abundant and can be transformed into syngas, alcohols, and other value-added chemicals, electrochemical reduction of CO₂ is more desirable than thermal reactions because of their potential advantages using a renewable energy source. Carbon dioxide electrochemical reduction reaction (CO₂ERR) is the conversion of carbon dioxide to chemical species using electrical energy. The products could be carbon monoxide (CO), ethylene (C₂H₄), formic acid (HCOOH), methane (CH₄), methanol (CH₃OH) and other hydrocarbons [1-3].

In aqueous electrolytes, the redox potential of hydrogen evolution is near to CO₂ERR reactions which act as a competitive reaction. An ideal catalyst would permit the reduction of the overpotential needed for CO₂ reduction as suggested in Figure 1, whereby kinetically, at least 1 V or more is needed to activate the large barriers of CO₂ERR which makes the process energetically inefficient. It is widely suggested that the

activation of CO₂ proceeds by means of a single electron reduction of CO₂ to the CO₂^{•-} radical intermediate from subsequent reduction. The standard potential for the formation of this radical anion is negative, i.e. -1.9 V vs standard hydrogen electrode (SHE) [4,5].

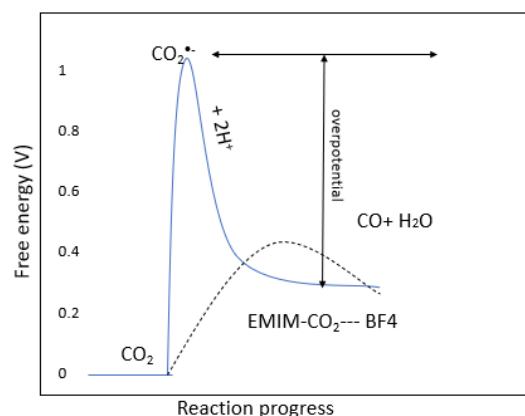


Fig. 1. Schematic illustration of the activation barriers for CO₂ reduction to CO in the presence (dashed line) and absence (solid line) of a catalytic specie [6].

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To find efficient electrocatalytic systems, many attempts have been done including using ionic liquid (IL)-based systems via modifying the class and components as the reaction medium and catalysts [7-9]. Nevertheless, to find the suitable catalysis system with high conversion efficiency remains as a challenge. Therefore, a clear understanding of the intrinsic characteristic of the electrochemical CO₂ reduction mechanism in ILs reaction systems is essential. The reaction usually occurs between the electrode and the electrolyte solvent in a very thin area (i.e. the electrical double-layer) [10-13].

To understand the relation of reactivity and chemical interactions between ILs and reaction components, few studies were reported in literature. The combinations between different metal electrodes and ILs were screened by Tanner et al. [14] where they observed that the cations activity coefficient follow in the order of [Bmim]⁺ > [Bmpyr]⁺ > [Emim]⁺ > [Pmim]⁺. A minor change in the performance of the reaction was found after modifying the imidazolium chain length. Alternately, the anions activity result was found as follow [Tf₂N]⁻ > [BF₄]⁻ > [FAP]⁻, which it could not demonstrate the correlation with the increasing solubility of CO₂ in different anions in the order of ([FAP]⁻ > [Tf₂N]⁻ > [BF₄]⁻). The authors highlighted that the ILs components are likely to change the electrical double-layer properties at the surface [14,15]. Experimental studies showed that the key role in the electrochemical reaction is governed by the cation species on the surface of the electrode which interact with the intermediate reaction and alter the properties of the electrical double-layer. In addition to the experimental efforts, theoretical simulations are focused primarily on ILs thermodynamic analysis and intermediate reactions [10, 16-19].

Vasilyev et al. reported a series of pyrazolium ionic liquids as co-catalysts for CO₂ electrochemical reduction leading to a significant decrease in the onset potential for the reduction of up to 500 mV and faradaic efficiencies of close to 100% [7]. Another study was reported by Rosen et al. who studied the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] solution at 18% concentration in CO₂ER reaction. The study suggested that the addition of water increases the catalytic activity of the IL hence reducing the overpotential [6].

To further elucidate the role of the ILs as co-catalysts, the aim of this study is to propose a correlation between the performance of ionic liquids as co-catalyst in CO₂ electrochemical reduction reaction with the lowest unoccupied molecular orbital (LUMO) energy level and the interaction energy as predicted by quantum chemical calculation using the conductor-like screening model for realistic solvents (COSMO-RS).

COSMO-RS is a quantum chemical calculation method to calculate the chemical potential differences of molecules in liquids developed by Klamt [20] and has gained interest in various application for prediction of thermodynamic properties and behavior of ionic liquids. The propose screening of potential ILs via a priori prediction using COSMO-RS will aid in the design for new catalysts and avoid unnecessary attempts.

2 Methods

First, the molecular structures of cations, anions, and their combinations (ILs) were optimized using Turbomole based on density functional theory to generate COSMO files using triple-zeta valence with polarization (TZVP) parametrization. The HOMO-LUMO energy levels were generated based on the optimized structures using TurboMole. Next, COSMO-RS was used to generate the σ -profile, and the interaction energy of the ionic liquids namely hydrogen bonding (H_{HB}), electrostatic interaction or misfit (H_{MF}), and van der Waals interaction (H_{vdW}). For this study, the ILs structures of the cations are: 1-ethyl-3-methylimidazolium (EMIM), 1,2-dimethyl-1H-pyrazol-2-ium (py12), 1,2,4-trimethyl-1H-pyrazol-2-ium (py124), 1,2,3-trimethyl-1H-pyrazol-2-ium (py123), 1,2,3,4-tetramethyl-1H-pyrazol-2-ium (py1234), 1,2,3,5-tetramethyl-1H-pyrazol-2-ium (py1235), 1,2,3,4,5-pentamethyl-1H-pyrazol-2-ium (py12345), as depicted in Figure 2.

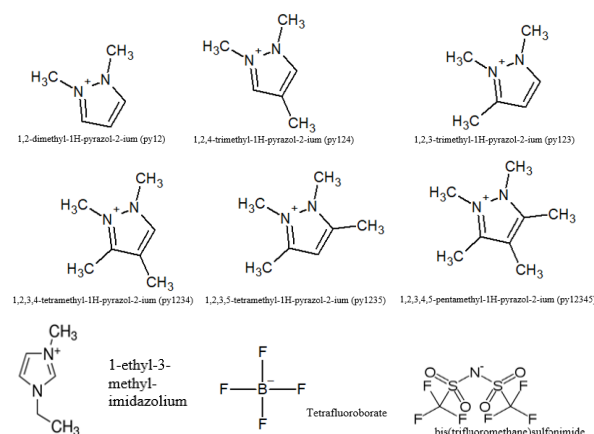


Fig. 2. Different cations and anions structures of the ILs used in this study.

To evaluate the effect of anions, two anions were compared namely bis(trifluoromethane)sulfonimide (TFSI) and tetrafluoroborate (BF₄). The reason for choosing these anions and cations is the availability of their CO₂ERR performance data from the literatures that are reported by Vasilyev and Rosen [6,7]. The LUMO values from experimental data [6,7] were calculated approximately based on the onset potential of reduction of the ionic liquids following Equation 1 [21].

$$E_{\text{LUMO}} = -(4.8 + E_{\text{onset}}^{\text{red}}) \text{ eV} \quad (1)$$

3 Results and Discussions

To evaluate the effect of the cations on the catalytic performance, a series of pyrazolium-based ionic liquids (Pz IL) from the work by Vasilyev are evaluated. A simple approximation is made where the effect of anions on the catalytic performance in the electrochemical reduction of the pyrazolium-based ionic liquids (Pz IL) are not taken in consideration. This can be validated because at negative potentials (where CO₂ reduction

reaction takes place), the cations form an adsorption layer at the electrode surface thus more dominant than the anion [7].

The σ -profile of the series of pyrazolium cations are presented in Figure 3. The σ -profile which represents the charge density profiles of the molecular surface can be divided into three important parts: hydrogen bond donor for $\sigma < -0.01$ e/nm², the non-polar region for $-0.01 < \sigma < +0.01$ e/nm², and hydrogen bond acceptor for $\sigma > +0.01$ e/nm². From Figure 3, it can be noticed that the order of hydrogen donation ability starting from the highest value is as follows: py12 > py124 > py123 > py1234 > py1235 > py12345.

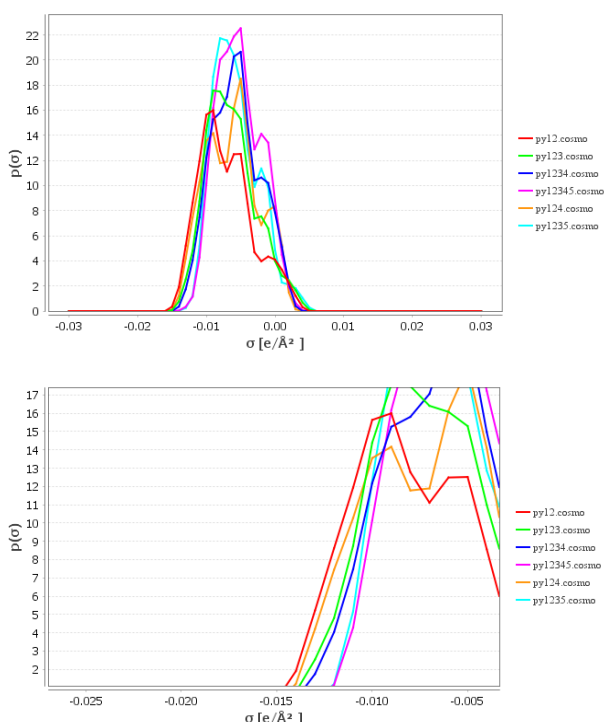


Fig. 3. (top) Sigma profile for pyrazolium ILs cations structures for py12, py123, py124, py1234, py1235 and py12345 and (bottom) zoom of the hydrogen donation region.

Vasilyev et al. reported the relationships between the structures and CO₂ electrochemical reaction activity [7] in the order of cations from the highest value as follows py12 > py124 > py123 > py1234 > py1235 > py12345. It is therefore following the same trend as the hydrogen donation properties. Therefore, it can be deduced that the higher the hydrogen donation properties the higher the catalysis activity of the ionic liquid towards CO₂ERR. To further elucidate this hypothesis, the interaction energies values namely hydrogen bonding (H_{HB}), electrostatic interaction or misfit (H_{MF}), and van der Waals interaction (H_{vdW}) for these structures were further estimated using COSMO-RS and the results are reported in Table 1.

Table 1. Different interaction energies values in kcal·mol⁻¹ generated by COSMO-RS for CO₂ and pyrazolium cations.

Compound	H _{MF}	H _{HB}	H _{vdW}
CO ₂	1.057	0.000	-2.548
Py12	2.68	-0.725	-6.053
Py123	3.055	-0.482	-6.810
Py124	3.106	-0.613	-6.970
Py1234	3.447	-0.394	-7.636
Py1235	3.465	-0.248	-7.598
Py12345	3.377	-0.217	-7.898

From Table 1, the negative sign indicates the attraction forces, whereby the Py12 has the highest hydrogen bond donor energy of -0.725 kcal·mol⁻¹ as compared to py12345 with a value of -0.217 kcal·mol⁻¹. It can be observed that for the different pyrazolium structures the hydrogen bond interaction energy is in the increasing order similar to the CO₂ER reaction activity as per reported by Vasilyev et al. [7]. The hydrogen bond interaction energy positively affects the catalysis activity which can be explained by the ability to reduce the strength of covalent bonding in CO₂ molecules and favoring the intermediate formation.

The LUMO energy levels for CO₂ and pyrazolium ILs are depicted in Figure 4 to study their effect towards the catalyst activity. From Figure 4, the order of the LUMO values from the lowest is as follow py12 < py124 < py123 < py1234 < py1235 < py12345. The same trend is observed for the calculated experimental LUMO values from the onset reduction of pyrazolium ILs reported by Vasilyev et al. [7] as shown in Table 2.

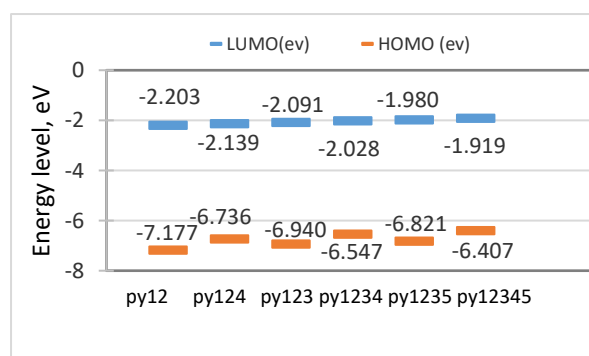


Fig. 4. Predicted HOMO-LUMO values of different structures of pyrazolium based cations from TurboMole.

Table 2. Computational and experimental LUMO values of pyrazolium cations.

Structure	Computational LUMO (eV)	Experimental LUMO (eV)	% deviation
py12	-2.20	-2.90	24.1379
py124	-2.14	-2.86	25.1748
py123	-2.09	-2.82	25.8865
py1234	-2.03	-2.76	26.4493
py1235	-1.98	-2.74	27.7372
py12345	-1.91	-2.72	29.7794

The slight increase in deviation percentage is because of the experimental reduction potentials were determined in presence of acetonitrile as solvent for the different ILs whereas the computational LUMO determination is based on pure cation of the pyrazolium ILs [7]. Despite that, the order of the LUMO values remain the same. Based on the experimental result, the order of the catalysis activity according to the structure, starting from the highest is $py12 > py124 > py123 > py1234 > py1235 > py12345$ which is the same order in decreasing LUMO values [7]. Thus, it can be deduced that the lower the LUMO energy level of the ionic liquid, the higher the catalytic activity in CO_2 ER reaction. This is consistent with the representation of LUMO energy level where it is associated with the tendency to receive electron. Hence, the lower the LUMO energy level the easier for the molecule to receive electron, thus increasing the catalytic activity and reducing the overpotential.

Furthermore, to investigate the overall effect of LUMO energy level and hydrogen bond (HB) interaction, a correlation between them has been developed as shown in Figure 5. It can be observed that strong linear relationship between LUMO values and hydrogen bond (HB) interactions energies with R-squared value of 0.9985 which means that the magnitude of hydrogen bond interaction energy increases when the LUMO value decreases and this grants a good catalytic property for CO_2 electrochemical reduction reaction. From previous studies, the ionic liquids have shown the ability to arrange on the silver electrode surface in a coplanar manner to form a double-layer [8][9]. Vasilyev et al. suggested that, the co-catalyst effect comes from the ion pair stabilization, ion interactions, and modifications in the local microenvironment [7]. They suggested that the nitrogen domain in the pyrazolium cation is the most charged region, and the substitution at the positions of C3 and C5 changes the system activity more than at the position of C4. They assumed that the CO_2^- intermediate interacts with the pyrazolium ring's positively charged region, which helps to stabilize the intermediate and reduce the reaction overpotential. However, in this present study, it can be seen that not only the ring has its own catalytic role, the intrinsic property of the LUMO energy level of the IL cation changes with the change of the alkyl substitution group position which could be the reason behind the catalytic efficiency.

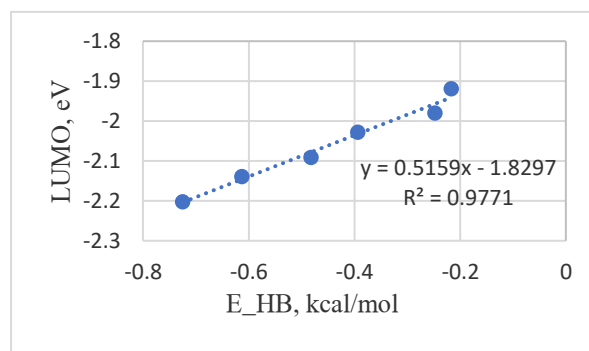


Fig. 5. The correlation between LUMO energy levels and hydrogen bond donor energy.

In another study, Buijs et al. [10] suggested that the LUMO of the ionic liquid is totally located on the cation. Therefore, the cation resistance to reduction mainly controls the stability of the ionic liquid reduction. They used experimental data from literatures [11-13] to study the effect of LUMO on the reduction resistance. Seven different cations were studied, and it was also found that the IL with the lowest LUMO value has the highest catalytic activity.

To further validate the hypothesis, the electrolyte system consists of pure IL 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] and [EMIM][BF₄] in aqueous solution at 18 wt% concentration was compared as shown in Table 3 and Table 4. From Table 4, it can be observed that the addition of water has indeed increased the hydrogen bond energies between the molecules, whereas other interaction energies remain unchanged. Rosen et al. reported that when using [EMIM][BF₄] as co-catalyst in CO_2 electrochemical reduction reaction, the addition of water increases the catalytic activity of the IL in terms of reducing the overpotential [6]. This further validate our correlation on increasing the hydrogen bonding to increase the catalytic activity. The hydrogen bond interaction between the cations and CO_2 may decrease the strength of covalent bond of carbon dioxide molecule, hence reducing the energy potential required.

Table 3. Interaction energies before addition of water.

Compound	mu	H_MF	H_HB	H_int
CO ₂	5.369	1.244	0.00000	-1.338
BF ₄	7.248	1.575	-1.259	-2.039
EMIM	5.112	3.726	-1.259	-4.407

Table 4. Interaction energies after addition of 18wt% water.

Compound	mu	H_MF	H_HB	H_int
CO ₂	5.503	1.243	0.00000	-1.338
BF ₄	6.695	1.495	-2.127	-2.039
EMIM	5.274	3.722	-1.387	-4.407
H ₂ O	4.208	0.337	-3.522	-4.477

4 Conclusion

COSMO-RS and TurboMole were used to highlight the effect of molecular interaction especially the hydrogen bond interactions and the LUMO energy level on the catalytic properties in CO₂ electrochemical reduction reaction. This was supported by experimental data from literatures. From this study, possible explanations have been highlighted. The first is the hydrogen bond interaction between the cations and CO₂ may weaken the strength of the covalent bonding of carbon dioxide molecule and decrease the strong linearity of CO₂ molecules, thus reducing the energy potential required. Secondly, the electrochemical reduction reaction favors ionic liquids with low LUMO energy levels values. Based on the correlation between hydrogen bond energy and LUMO value, a strong linear relationship is obtained, whereby as the magnitude of the hydrogen bond interaction energy increases, the LUMO value decreases. The ILs show good potential as co-catalyst because of the high solubility of CO₂ solubility in different anions and the low LUMO values of different cations which associated with an increase in the hydrogen bond interaction energy.

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