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Communication

Alkali metal cation effects on electrocatalytic CO₂ reduction with iron porphyrins

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ABSTRACT

The electrocatalytic CO₂ reduction reaction (CO₂RR) has attracted increasing attention in recent years. Practical electrocatalysis of CO₂RR must be carried out in aqueous solutions containing electrolytes of alkali metal cations such as sodium and potassium. Although considerable efforts have been made to design efficient electrocatalysts for CO₂RR and to investigate the structure–activity relationships using molecular model complexes, only a few studies have been investigated the effect of alkali metal cations on electrocatalytic CO₂RR. In this study, we report the effect of alkali metal cations (Na⁺ and K⁺) on electrocatalytic CO₂RR with Fe porphyrins. By running CO₂RR electrocatalysis in dimethylformamide (DMF), we found that the addition of Na⁺ or K⁺ considerably improves the catalytic activity of Fe chloride tetrakis(3,4,5-trimethoxyphenyl)porphyrin (**FeP**). Based on this result, we synthesized an Fe porphyrin **18C6-FeP** bearing a tethered 1-aza-18-crown-6-ether (**18C6**) group at the second coordination sphere of the Fe site. We showed that with the tethered **18C6** to bind Na⁺ or K⁺, **18C6-FeP** is more active than **FeP** for electrocatalytic CO₂RR. This work demonstrates the positive effect of alkali metal cations to improve CO₂RR electrocatalysis, which is valuable for the rational design of new efficient catalysts.

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Electrocatalytic reduction of CO₂ is an effective way to transform greenhouse gas into fuels and value-added chemicals [1–7]. Highly efficient electrocatalysts are required for CO₂RR. In the past decade, extensive efforts have resulted in the identification of a variety of first-row transition metal complexes, including those of Mn [8–11], Fe [12–14], Co [15–18], Ni [19,20], and Cu [21–23], as electrocatalysts for CO₂RR. By studying these molecular catalysts, fundamental knowledge of structure–activity relationships has been obtained. For exam-

ple, intramolecular proton relay sites and electrostatic interaction substituents can significantly improve catalytic efficiency for CO₂RR [24–27]. However, despite these achievements, the effect of alkali metal cations on CO₂RR has rarely been studied [28], although practical CO₂RR electrocatalysis is required to be carried out in aqueous solutions containing electrolytes of alkali metal cations, such as sodium or potassium [29–32].

Among the molecular catalysts, Fe porphyrins are highly active and selective for electrocatalytic CO₂-to-CO conversion

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[33–42]. Importantly, the rigid and stable coordination structures of porphyrins, as well as the accessibility to install various functional groups on their macrocycle backbones, provide an ideal platform to investigate structure–activity relationships for CO₂RR [43–48]. With these considerations, using Fe porphyrins as molecular model complexes, we herein report the effect of alkali metal cations, including Na⁺ and K⁺, on electrocatalytic CO₂RR. We found that the catalytic activity of **FeP** (Fig. 1(a)) increased in the presence of free Na⁺ or K⁺ in DMF. Using Fe porphyrin **N18C6-FeP** (Fig. 1(a)), which bears a tethered 1-aza-18-crown-6-ether (**N18C6**) group to bind Na⁺ or K⁺ at the second coordination sphere of the Fe site, the electrocatalytic CO₂RR activity was further improved. This work demonstrates the positive effect of alkali metal cations on improving CO₂RR electrocatalysis and is therefore valuable for the rational design and development of efficient catalysts for CO₂RR.

First, the **FeP** complex was synthesized and characterized (details are described in the Supporting Information). The UV-Vis absorption spectrum of **FeP** exhibits characteristic Soret and Q bands at 421 and 573 nm, respectively (Fig. S22(a)). The identity and purity of **FeP** were further confirmed using high-resolution mass spectrometry (HRMS), which detected an ion at a mass-to-charge ratio of 1028.2911 (Fig. S4). This value matches the calculated value of 1028.2927 for the monovalent cation [**FeP**-Cl]⁺ with the expected isotopic distribution. Importantly, single crystals of **FeP** suitable for single-crystal X-ray diffraction measurements were obtained. Crystallographic studies showed that **FeP** crystallized in the triclinic *P* $\bar{1}$ space group with *V* = 1721.2(4) Å³ and *Z* = 1. The thermal ellipsoid plot of the X-ray structure of **FeP** is shown in Fig. 1(b). In the crystal structure, the **FeP** molecule is located at the crystallographically required inversion center. As a consequence, only half of the molecule was found in the asymmetric unit. The Fe ion is incorporated into the porphyrin ligand through four N atoms and has square-pyramidal coordination geometry, with

Fig. 1. (a) Molecular structures of **FeP** and **N18C6-FeP**; (b) Thermal ellipsoid plot (50% probability) of the X-ray structure of **FeP**. Hydrogen atoms are omitted for clarity.

the four N atoms of the porphyrin macrocycle defining the equatorial plane and with a chloride ligand occupying one axial site. The average Fe–N distance is 2.117(4) Å, and the Fe–Cl distance is 2.240(3) Å. Because the Fe ion was domed out by the N₄-equatorial plane due to the binding with the chloride ion, the FeCl unit was positionally disordered at both the up and down sides of the porphyrin plane (Fig. S5). The Fe^{III} oxidation state was suggested based on the bond valence sum and charge balance calculations.

The electrocatalytic features of **FeP** for CO₂RR were measured in 0.1 M Bu₄N(PF₆) DMF using a glassy carbon working electrode. Cyclic voltammetry (CV) of **FeP** under argon displayed one quasi-reversible redox wave at –0.63 V vs ferrocene

Rui Cao (College of Chemistry and Chemical Engineering, Shaanxi Normal University) received the SPP/JPP Young Investigator Awards from International Society of Porphyrins and Phthalocyanines in 2020. Professor Rui Cao received his B.S. degree (2003) in chemistry from Peking University in Beijing, China and his Ph.D. degree (2008) from Emory University in Atlanta, Georgia, USA with Professor Craig L. Hill. He worked as a Postdoctoral Fellow (2008–2009) at Emory University and as the Dreyfus Postdoctoral Fellow (2009–2011) at Massachusetts Institute of Technology with Professor Stephen J. Lippard. In 2011, he became a professor at Renmin University of China, and transferred to Shaanxi Normal University in 2014. His main research interests include bioinorganic chemistry and molecular electrocatalysis for energy-related small molecule activation reactions. Some of his recent progresses using metal porphyrins as catalysts include: (1) demonstrating and controlling homolytic versus heterolytic hydrogen evolution reaction through steric effects, (2) developing porphyrin-appended water-soluble polymers as bioinspired catalysts for both electro- and photocatalytic hydrogen evolution reactions, (3) achieving low overpotential water oxidation at neutral pH and controlling water oxidation selectivity to either O₂ or H₂O₂ with a copper porphyrin, (4) developing an asymmetrical dinuclear cobalt porphyrin for highly efficient and selective oxygen reduction, and (5) engineering carbon materials and metal oxides with molecular catalysts for efficient molecular electrocatalysis. Since 2011 when starting his independent research, Professor Cao has published more than 100 peer-reviewed papers. He joined the editorial Board of *Chin. J. Catal.* since 2020, *Chem. Soc. Rev.* since 2019, and *Chin. Chem. Lett.* since 2017.

and two reversible redox waves at -1.50 and -2.14 V vs. ferrocene (Fig. 2(a), all the potentials reported herein are referenced to ferrocene). These waves were attributed to the formal $\text{Fe}^{\text{III/II}}$, $\text{Fe}^{\text{II/I}}$, and $\text{Fe}^{\text{I/0}}$ redox couples, respectively. Dissociation of the axial chloride ligand upon the reduction of the Fe ion results in relatively poor reversibility of the $\text{Fe}^{\text{III/II}}$ redox couple. The $\text{Fe}^{\text{II/I}}$ reduction peak current displayed a linear relationship with the square root of the scan rate (Fig. 2(b)), indicating that the **FeP** molecules can freely diffuse under non-catalytic conditions. Linear sweep voltammetry (LSV) of **FeP** under CO_2 with 10 mM of H_2O showed that the $\text{Fe}^{\text{I/0}}$ redox wave became a large catalytic wave (Fig. 2(c)). It was determined that this catalytic wave corresponded to the reduction of CO_2 rather than the reduction of protons because the same LSV measurement under argon with 10 mM H_2O displayed a very small current at the same potentials. As shown in Fig. 2(d), the catalytic currents increased linearly with **FeP**, suggesting a first-order dependence of the catalytic rate on the concentration of **FeP**. Controlled potential electrolysis confirmed the stability of **FeP** functioning as a CO_2RR electrocatalyst, showing stable currents during electrolysis at -2.25 V (Fig. S23(a)) and almost identical UV-Vis spectra of **FeP** before and after electrolysis (Fig. S23(b)). The evolved CO was analyzed using gas chromatography, determining a Faradaic efficiency of 95% for CO_2 -to-CO conversion (Fig. S28).

After confirming the molecular nature of **FeP** for electrocatalytic CO_2RR , we investigated the effect of alkali metal cations (Na^+ and K^+) on CO_2RR using **FeP** in DMF. As shown in Figs. 3(a) and 3(b), with the addition of Na^+ and K^+ , the catalytic currents for CO_2RR increased in intensity. For example, the catalytic current with 20 equivalents of Na^+ is 1.4 times that without Na^+ , whereas the catalytic current with 20 equivalents of K^+ is 3.8 times that without K^+ . Importantly, the LSVs of **FeP** under argon with the addition of these alkali metal cations showed negligible current increase (Fig. S24), indicating that

Fig. 2. (a) CV of 0.5 mM **FeP** in DMF under argon at a scan rate of 100 mV s^{-1} ; (b) Plot of the $\text{Fe}^{\text{II/I}}$ reduction peak current against the square root of the scan rate. The concentration of **FeP** was 0.5 mM; (c) LSVs of 1.0 mM **FeP** in DMF under argon and under CO_2 with 10 mM H_2O ; (d) LSVs of different concentrations of **FeP** in DMF under CO_2 with 10 mM H_2O . Inset: the plot of catalytic current against the concentration of **FeP**, showing a linear relationship.

Fig. 3. LSVs of 0.5 mM **FeP** in DMF under CO_2 with the addition of Na^+ (a) and K^+ ions (b).

the current increase under CO_2 was due to improved CO_2RR . Notably, compared to Na^+ ions, the addition of K^+ ions resulted in more significant improvements in the catalytic currents. This is likely caused by the faster migration of K^+ ions than Na^+ in solution, as K^+ ions have a weaker hydration/solvation effect.

Based on these results, we designed and synthesized an Fe porphyrin **N18C6-FeP** by tethering an **N18C6** group onto the porphyrin backbone (Fig. 1(a)). We propose that the **N18C6** group is able to bind Na^+ and K^+ ions, which further improves the electrocatalytic CO_2RR through intramolecular interactions with the alkali metal cations. The detailed synthesis and characterization of **N18C6-FeP** are described in the Supporting Information. The UV-Vis absorption spectrum of **N18C6-FeP** exhibits characteristic Soret and Q bands at 413 and 570 nm, respectively (Fig. S22(b)), which are very close to those of **FeP**. The identity and purity of **N18C6-FeP** were confirmed by HRMS, showing an ion at a mass-to-charge ratio of 1303.4458 (Fig. S21). This value matches the calculated value of 1303.4449 for the monovalent cation $[\text{N18C6-FeP-Cl}]^+$ with the expected isotopic distribution. These results suggest that **N18C6-FeP** and **FeP** have similar coordination structures, except that the former bears a tethered **N18C6** group.

The redox features of **N18C6-FeP** are very close to those of **FeP** in DMF under argon (Table 1), displaying one quasi-reversible redox wave at -0.60 V and two reversible redox waves at -1.48 and -2.12 V (Fig. 4(a)). The linear relationship between the $\text{Fe}^{\text{II/I}}$ reduction peak current and square root of the scan rate suggests that **N18C6-FeP** can also freely diffuse under non-catalytic conditions (Fig. 4(b)). Similar to **FeP**, the $\text{Fe}^{\text{I/0}}$ redox wave of **N18C6-FeP** became a large catalytic wave under CO_2 in the presence of 10 mM H_2O as the proton source (Fig. 4(c)). Control experiments under argon with 10 mM H_2O displayed a very small current at the same potentials, confirming the catalytic reduction of CO_2 rather than reduction of protons. The catalytic current increased linearly with the increase in **N18C6-FeP** concentration (Fig. 4(d)), indicating the molecular nature of this catalysis. During electrolysis at -2.23 V under CO_2 , stable currents were maintained (Fig. S25(a)) and the UV-Vis spectra of **N18C6-FeP** before and after electrolysis were

Table 1
Reduction potentials of **N18C6-FeP** and **FeP** in DMF.

Complex	$E_{1/2}$ (V vs. ferrocene)		
	$\text{Fe}^{\text{III/II}}$	$\text{Fe}^{\text{II/I}}$	$\text{Fe}^{\text{I/0}}$
FeP	-0.63	-1.50	-2.14
N18C6-FeP	-0.60	-1.48	-2.12

Fig. 4. (a) CV of 0.5 mM **N18C6-FeP** in DMF under argon at a scan rate of 100 mV s⁻¹; (b) Plot of the Fe^{II/I} reduction peak current against the square root of the scan rate. The concentration of **N18C6-FeP** was 0.5 mM; (c) LSVs of 1.0 mM **N18C6-FeP** in DMF under argon and under CO₂ with 10 mM H₂O. (d) LSVs of different concentrations of **N18C6-FeP** in DMF under CO₂ with 10 mM H₂O. Inset: plot of catalytic current against the concentration of **N18C6-FeP**, showing a linear relationship.

almost identical (Fig. S25(b)). Gas chromatography analysis demonstrated a Faradaic efficiency of > 92% for CO production (Fig. S29). These results confirm that **N18C6-FeP** is also stable for electrocatalysis of CO₂-to-CO conversion.

Next, we studied the catalytic behavior of **N18C6-FeP** with the addition of Na⁺ and K⁺ ions. As shown in Figs. 5(a,b), the catalytic CO₂RR currents increased in intensity by 3.4 times with 20 equivalents of Na⁺ (Fig. 5(a)) and by 4.2 times with 20 equivalents of K⁺ (Fig. 5(b)). Moreover, with the same concentrations of Na⁺ and K⁺, **N18C6-FeP** exhibited larger catalytic currents than **FeP** (Fig. 5(c)). Bulk electrolysis of **N18C6-FeP** confirmed the production of CO with Na⁺ and K⁺, suggesting that the addition of alkali metal cations improved the electro-

Fig. 5. LSVs of 0.5 mM **N18C6-FeP** in DMF under CO₂ with the addition of Na⁺ (a) and K⁺ (b). Conditions: 0.1 M Bu₄N(PF₆), 100 mV s⁻¹ scan rate, 10 mM H₂O. (c) Catalytic CO₂RR currents with **FeP** and **N18C6-FeP** in the absence and in the presence of 20 equivalents of Na⁺ and K⁺. (d) ¹H NMR titration studies of **N18C6** in CD₃CN, showing the downfield shifts of the peak at 3.49 ppm with the addition of Na⁺ and K⁺.

catalytic CO₂RR activity but had negligible influence on the selectivity. We propose that these alkali metal cations can stabilize the Fe–CO₂ adduct through electrostatic interactions, leading to improved activity. To confirm that the **N18C6** group can bind the alkali metal cations, we performed titration experiments using ¹H NMR spectroscopy [49,50]. In CD₃CN, with the addition of Na⁺ (Fig. S26) and K⁺ (Fig. S27), the ¹H NMR peaks of **N18C6** displayed considerable downfield shifts, indicating the presence of coordination interactions between **N18C6** and the alkali metal cations. In addition, we carried out titration experiments in CD₃CN in the presence of 0.1 M Bu₄N(PF₆). As shown in Fig. 5(d), the downfield shifts of the ¹H NMR peaks of **N18C6** reached saturation with > 10 equivalents of Na⁺ and K⁺. Interestingly, although **N18C6** was shown to have comparable binding affinity with Na⁺ and K⁺ (i.e., similar saturation equivalents), **N18C6-FeP** displayed a more significant improvement in the catalytic CO₂RR currents with Na⁺ than with K⁺. We rationalized that free K⁺ ions migrate faster than Na⁺ ions in solution, resulting in higher catalytic activity for **FeP** with K⁺ ions. However, for **N18C6-FeP**, the tethered **N18C6** group can bind Na⁺ and K⁺ ions with comparable binding affinities, and thus their catalytic CO₂RR activities are at similar levels. Therefore, the improvement with Na⁺ is more significant for **N18C6-FeP** in CO₂RR electrocatalysis. This is strong evidence to support the role of the tethered **N18C6** group in improving catalytic CO₂RR.

In summary, we report the effect of alkali metal cations on electrocatalytic CO₂RR using Fe porphyrins. Our results show that both Na⁺ and K⁺ ions can enhance the catalytic activity of **FeP**, and that the improvement with free K⁺ is larger than that with free Na⁺. For **N18C6-FeP**, which bears a tethered **N18C6** group to bind Na⁺ and K⁺ ions, we show further improved catalytic CO₂RR. In particular, by binding Na⁺ for intramolecular catalysis, the CO₂RR activity can be significantly improved than that with free Na⁺ ions. Therefore, this work provides new insights into the design of efficient CO₂RR catalysts, which will be valuable for designing catalysts for other small molecule activation reactions.

Notes

The authors declare no competing financial interest.

Electronic supporting information

Supporting information is available in the online version of this article

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Alkali metal cation effects on electrocatalytic CO₂ reduction with iron porphyrins

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Using an iron porphyrin bearing a tethered ^N18C6 group, the effect of alkali metal cations, such as sodium and potassium, on improving electrocatalytic CO₂RR is demonstrated.

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碱金属阳离子对铁卟啉电催化CO₂还原的影响

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摘要: 电催化CO₂还原反应(CO₂RR)可以有效地将温室气体转化为燃料或高附加值的化学品, 从而缓解目前人类所面临的环境问题和能源危机, 其中开发高效的电催化剂是至关重要的环节。近年来, 研究者设计了多种高效的过渡金属配合物(包括Mn, Fe, Co, Ni和Cu)用作CO₂RR分子电催化剂, 并研究了其中的构效关系, 例如, 在分子内修饰质子给体取代基或电荷取代基可以显著提高CO₂RR的催化效率。而电催化CO₂RR的实际应用要在含有碱金属阳离子(例如, Na⁺和K⁺)的电解质水溶液中进行, 但在已有报道中, 很少有关于碱金属阳离子对CO₂RR的影响。在众多的分子催化剂中, 铁卟啉可以以较高的催化活性和选择性实现CO₂到CO的转化。重要的是, 卟啉环的刚性结构、稳定的配位环境及其骨架上官能团的易于修饰性成为研究CO₂RR的构效关系的理想分子模型。基于以上考虑, 本文以铁卟啉配合物为分子模型, 研究了碱金属阳离子Na⁺和K⁺对电催化CO₂RR的影响。

首先, 本文合成了简单的A4型铁卟啉化合物四-(3,4,5-三甲氧基苯基)-铁卟啉(**FeP**)。并采用核磁共振、质谱分析、单晶衍射等表征手段对化合物进行了表征, 在含有电解质的DMF溶液中测试其电催化CO₂还原性能。实验结果表明, **FeP**可以实现高效的电催化CO₂还原, 催化电流随**FeP**的浓度呈线性增加, 说明催化反应速率与催化剂浓度呈一级反应速率关系。较长时间的恒电压电解实验以及电解前后化合物的紫外-可见光谱证实了**FeP**的稳定性。通过气相色谱对产物进行分析, CO为主要产物, 法拉第效率为95%。以上结果均表明, **FeP**是一个优良的分子催化剂。在此基础上, 本文还发现加入Na⁺和K⁺均可以显著提升催化活性, 而K⁺的加入使催化电流的提升更加显著, 这可能是由于K⁺在溶液中的迁移速度比Na⁺更快。基于此实验现象, 本文通过在**FeP**的第二配位层修饰1-氨-18-冠-6-醚官能团(**N18C6**), 合成了**N18C6-FeP**化合物。结果表明, 由于**N18C6**与Na⁺/K⁺之间的配位作用, 使得**N18C6-FeP**比**FeP**具有更好的电催化CO₂RR活性。研究表明, 催化活性的提升归因于碱金属阳离子能够通过静电相互作用稳定Fe-CO₂中间体。¹H NMR谱证实了**N18C6**基团的确能够螯合碱金属阳离子。本文研究证明了碱金属阳离子对改善电催化CO₂RR的积极作用, 对于进一步深入了解CO₂RR催化反应机理和未来合理的设计高效催化剂也都具有重要意义。

关键词: 二氧化碳还原; 分子电催化; 碱性金属阳离子效应; 铁卟啉; 构效关系

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