CO₂电化学还原过程中电解质研究现状及趋势

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摘要 随着工业化的迅速发展, 大气中CO₂含量逐步增加并造成日益严重的环境问题. 合理利用CO₂并将其转变为有用的燃料或化学品, 成为国际学术界和工业界共同关注的热点. 电化学还原CO₂因反应条件温和、反应产物可调, 且利用可再生或分布式电能, 而受到研究者青睐. 在CO₂电化学还原体系中, 电解质为CO₂分子的传输及电化学还原提供了重要的环境, 且作为导电介质, 构成了闭合电路. 研究表明, 电解质种类、浓度和pH等均会改变电极表面反应环境的性质, 影响产物的电流密度和选择性, 在CO₂电化学还原过程中起到重要的作用. 本文针对国内外CO₂电化学还原过程中各类电解质的研究现状及性能等进行了论述, 重点总结了碱金属盐和离子液体两类电解质对电化学还原CO₂反应的电流密度、产物选择性和过电势等的影响, 分析了CO₂还原生成不同产物的机理, 展望了CO₂电化学还原电解质体系的研究和发展趋势.

关键词 CO₂, 电化学还原, 碱金属盐, 离子液体, 反应机理

随着社会经济的发展及人类活动的影响, 大气中CO₂浓度逐步升高. 截至2019年, 大气中CO₂浓度已达414.7 ppm(parts per million, <http://www.jsdthb.com/info/577.html>), 预计到2100年CO₂浓度可达600 ppm. 大气中CO₂含量增加会引起温室效应、冰川融化、海平面上升等问题, 将CO₂转化为有用的液体燃料或化学品, 是从根本上减缓温室效应和减少化石燃料用量的重要途径, 具有重大意义^[1,2]. 目前CO₂转化利用的方法包括热化学、生物化学、电化学、光化学等^[3-6], 其中电化学还原CO₂因在常温常压条件下进行、产物种类多样, 且可利用可再生或分布式能源等, 受到广泛关注. 但要实现CO₂高效转化, 还存在许多挑战和难点: 阴极存在析氢竞争反应, 导致产物选择性降低; CO₂分子稳定, 得电子生成CO₂⁻($E(\text{CO}_2/\text{CO}_2^-) = -1.9 \text{ V vs. NHE, pH } 7$)过电

势高. 近年来, 大量研究者通过改变电极材料、电解池和电解质等, 来抑制析氢反应和提高CO₂还原产物的法拉第效率及电流密度^[7-11]. 研究表明, 溶液中电解质不同会极大地影响CO₂还原性能. 如在常规水溶液中利用碱金属Li⁺或Cs⁺盐作为电解质时, CO₂还原活性呈现1~3个数量级的差别, 主要是因为碱金属阳离子半径不同, 溶剂化程度也有差异, 改变了电极表面外赫姆霍兹层(outer Helmholtz plane, OHP)的pH、电场强度等, 最终影响CO₂还原产物的选择性及电流密度^[12-14]. 又如将离子液体1-乙基-3-甲基咪唑四氟硼酸盐([Emim][BF₄])作为电解质, 相同条件下CO₂还原生成CO的电流密度是KHCO₃水溶液体系的14倍. CO₂还原性能提高的主要原因是离子液体阴阳离子与CO₂存在氢键、静电或其他化学作用, 提高了CO₂溶解能力, 在电极协同作用

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下改变CO₂分子结构,降低了还原反应过电势^[15~18]。目前关于CO₂电化学还原的综述已有多篇报道,但主要侧重于水溶液中铜基或其他催化剂的设计合成及还原机理^[19~25]、离子液体体系中CO₂还原性能^[26~29]和电解池设计^[30~32],而有关电解质的综述报道较少。鉴于电解质在CO₂电化学还原中所起到的重要作用,本文则重点介绍碱金属盐和离子液体这两类电解质体系,探讨电解质体系对CO₂电化学还原性能和产物的影响规律及还原机理,并展望了电解质体系的发展趋势和方向。

1 碱金属盐电解质的研究进展

1.1 电化学还原CO₂产物变化规律

有研究发现,在水溶液体系中碱金属阳离子的种类会明显影响CO₂还原反应的电流密度和还原产物分

布。表1梳理了不同碱金属碳酸氢盐水溶液对CO₂还原活性的影响。Hori和Murata^[33]以多晶铜为电极,采用不同碱金属的碳酸氢盐水溶液为电解质,研究了一价碱金属阳离子种类对CO₂还原产物选择性的影响,发现当阳离子从Li⁺变为Cs⁺,即阳离子尺寸增大时,溶液pH增加且C₂产物与C₁产物(C₂/C₁)法拉第效率比值由0.16增至1.88,而H₂法拉第效率从60.5%降到24.4%,表明大尺寸阳离子有利于提高C₂产物选择性。Ager课题组^[34]研究了K⁺和Cs⁺的碳酸氢盐电解质中,不同方法制备的Cu电极上CO₂还原反应的活性,发现电解质含Cs⁺时,多碳产物的法拉第效率和电流密度均大于K⁺,说明电解质中含Cs⁺较K⁺表现出更高的多碳产物还原效果。同时研究了低指数晶面Cu(110)和Cu(111)上碱金属阳离子对反应活性的影响,发现随阳离子尺寸增大,反应电流密度逐渐增大,且HCOOH和CH₂=CH₂的法拉第效率明显

表1 不同碱金属碳酸氢盐水溶液对CO₂还原活性影响^{a)}

Table 1 Effect of various alkali metal bicarbonate electrolytes on activity of CO₂ electrochemical reduction

电极	电解质	法拉第效率(%)					电势(V)	电流密度(mA/cm ²)	文献
		H ₂	CO	HCOOH	CH ₄	C ₂ H ₄			
Cu	LiHCO ₃	60.5	-	4.7	32.2	5.2	-1.45 vs. SHE	5.0	[33]
Cu	NaHCO ₃	25.1	1.0	7.0	55.1	12.9	-1.45 vs. SHE	5.0	[33]
Cu	KHCO ₃	14.5	0.5	8.3	32.0	30.3	-1.39 vs. SHE	5.0	[33]
Cu	CsHCO ₃	24.4	2.4	15.8	16.3	30.5	-1.38 vs. SHE	5.0	[33]
电还原Cu	KHCO ₃	26.9	0.5	2.3	9.2	38.4	-1.0 vs. RHE	9.0	[34]
电还原Cu	CsHCO ₃	23.7	0.5	1.9	0.9	45.0	-1.0 vs. RHE	13.5	[34]
电沉积Cu	KHCO ₃	32.0	0.9	3.4	7.8	38.6	-1.0 vs. RHE	8.8	[34]
电沉积Cu	CsHCO ₃	25.0	0.6	2.1	2.8	43.1	-1.0 vs. RHE	13.0	[34]
Cu纳米线	KHCO ₃	42.6	0.4	5.8	2.1	29.1	-1.0 vs. RHE	8.6	[34]
Cu纳米线	CsHCO ₃	34.8	0.3	1.7	0.1	37.3	-1.0 vs. RHE	12.7	[34]
纳米结晶Cu	KHCO ₃	76.4	0.2	0.6	-	9.9	-1.0 vs. RHE	25.0	[34]
纳米结晶Cu	CsHCO ₃	74.6	0.1	0.3	-	11.8	-1.0 vs. RHE	27.5	[34]
Cu	LiHCO ₃	86	0.5	0.5	6.2	1.5	-1.0 vs. RHE	2.4	[36]
Cu	NaHCO ₃	66.3	0.7	1.5	17.7	5.5	-1.0 vs. RHE	2.6	[36]
Cu	KHCO ₃	55.1	1.7	4.7	15.3	10.2	-1.0 vs. RHE	3.0	[36]
Cu	RbHCO ₃	32.2	2.3	2.7	13.2	24.4	-1.0 vs. RHE	4.0	[36]
Cu	CsHCO ₃	31.1	0.9	1.7	9.4	31.1	-1.0 vs. RHE	4.8	[36]
Ag	LiHCO ₃	44.2	55.8	-	-	-	-1.0 vs. RHE	2.0	[36]
Ag	NaHCO ₃	33.8	66.2	-	-	-	-1.0 vs. RHE	2.8	[36]
Ag	KHCO ₃	14.6	85.4	-	-	-	-1.0 vs. RHE	4.1	[36]
Ag	RbHCO ₃	11.9	88.1	-	-	-	-1.0 vs. RHE	4.7	[36]
Ag	CsHCO ₃	9.8	90.2	-	-	-	-1.0 vs. RHE	5.5	[36]

a) “-”代表无数据

增加^[35]. Bell课题组^[36]也在Ag表面上开展类似工作,发现当电解质从Li⁺盐变为Cs⁺盐, CO法拉第效率从55.8%提高到90.2%.

Kyriacou课题组^[37]研究了不同化合价的金属阳离子对CO₂反应活性的影响,以Cu-Sn-Pb为例,发现低电位下含La³⁺盐体系的还原速率是含Na⁺盐的2倍,产物CH₃CHO的法拉第效率由2.6%增加到17.6%, CH₄的法拉第效率从3.6%降低到2.3%,且发现溶液中CO₂还原速率随着阳离子表面电荷数(阳离子电荷数/阳离子球体直径)的增加而增加.但未来还需利用原位表征技术和模拟计算等手段,探究阳离子的表面电荷与还原速率之间的关系.

1.2 电化学还原CO₂的影响机理

电解质中碱金属阳离子种类对CO₂还原反应活性有很大影响,但影响机理有待深入研究. Murata和Hori^[33]基于Frumkin理论^[12]针对碱金属阳离子尺寸增大、多碳产物法拉第效率增加这一现象进行了分析,提出阳离子特异性吸附与OHP电势理论模型.在负电势条件下进行CO₂还原反应时,阴极表面带有负电荷,可通过库伦力或共价键作用特异性吸附阳离子.当吸附的阳离子半径越大,即水化半径越小,越易吸附在电极表面,则OHP电势的正移程度也越大,相应的电极表面吸附的氢质子浓度会降低,而近电极表面的高pH环境有利于生成多碳产物.阳离子的特异性吸附与OHP电势理论模型也被其他学者所认同^[38,39].然而,Janik课题组^[40]利用密度泛函理论(DFT)计算了常压下过渡金属电极表面上阳离子的吸附电势,发现了不同的现象,即碱金属阳离子在Pt(111)和Pd(111)电极表面发生低覆盖率的特异性吸附时(Li⁺的特异性吸附电势-2.63 V vs. NHE; Cs⁺的特异性吸附电势-2.44 V vs. NHE),阳离子的吸附电势远高于析氢反应电势,表明阳离子并非特异性吸附在电极表面.同时,Marković课题组^[41]和Yang课题组^[42]在碱金属电解质中进行氧还原反应时,发现碱金属阳离子与电极表面之间为非共价相互作用,因此需进一步探究碱金属阳离子影响CO₂电化学还原的机理.

直到2016年, Bell课题组^[36]在传质过程为速控步骤的前提下,提出了碱金属阳离子主要作为缓冲溶剂的理论.以Ag或Cu为电极, CO₂电化学还原过程中的碱金属阳离子主要作为缓冲溶剂而降低近电极表面pH,以增加CO₂的溶解度,减小浓差极化,促进CO₂还原反应

(图1).其原理是在外加电位作用下,阳离子向阴极迁移,导致溶剂化阳离子与阴极之间的静电相互作用增强,而阳离子尺寸越大,近电极表面阳离子水解的pK_a值越小,若pK_a低于邻近溶液pH,溶剂化的碱金属离子会释放H⁺作缓冲剂.学者进一步利用原位衰减全反射表面增强红外吸收光谱技术间接测量表面pH,发现CO₂传质控制时,近电极表面的阳离子主要是作为缓冲溶剂^[43,44].之后Ager课题组^[35,45]对传质过程并非速控步骤,碱金属阳离子尺寸增大促进CO₂还原的机理进行了探究,研究表明阳离子会在电极表面产生界面电场,稳定在电极表面产生的中间体,促进C-C偶联反应. Bell课题组^[35]对电极表面进行DFT计算,表明阳离子在OHP上会产生界面电场.电场的强度与阳离子尺寸有关,阳离子尺寸增大时,在电极表面积累的阳离子数目增多,局部电场强度增大.电极表面电场的产生降低了*CO₂吸附能量,有利于CO和HCOOH产物的生成,且电场与中间态之间存在静电相互作用,可降低形成*OCCO或*OCCHO的过电势,从而有利于多碳产物的形成. Chan课题组^[46]基于均匀静电场方法和修正后的Poisson-Boltzmann电解质分布模型^[47]进行的模拟计算也验证了阳离子种类会改变电极表面的电场强度,进而改变CO₂的反应活性的理论,且模拟计算结果与Ag电极表面还原生成CO、Cu表面生成多碳产物等实验检测到的数据一致.基于上述结果提出通用的碱金属盐电解质筛选原则,即选用较小水化半径的金属阳离子,最大限度地提高电场强度,从而提高CO₂还原反应活性.

2 离子液体电解质的研究进展

近年来,离子液体作为特殊的有机盐和非水电解质,因具有CO₂溶解度高、结构可调、蒸汽压低和电位窗口宽等独特的物化性质,在CO₂电化学还原反应中展现明显的优势.许多研究利用离子液体作为电解质,将CO₂还原生产CO、HCOOH和甲醇等不同产物.表S1总结了近年来离子液体电解质对CO₂还原活性的影响.

2.1 CO₂电化学还原制CO过程中离子液体电解质

迄今已报道了多种常规和功能离子液体在电化学还原CO₂中的应用. Masel课题组^[48]在Ag电极上,以[Emim][BF₄]为电解质,低电位下获得选择性高达96%的CO,推测在电解过程中形成了[Emim]-CO₂-[BF₄]⁻的复合中间态,显著降低了反应过电势(图2). Brennecke课题组^[49]在Pb电极上,以四乙基高氯酸铵(TEAP)为电

图1 (网络版彩色)Ag电极表面阳离子对CO₂还原反应的影响^[36]. (a) 赫姆霍兹层和溶液本体Li⁺和Cs⁺水解的pK_a值; (b) 边界层和溶液本体的pH和CO₂浓度分布; (c) Ag表面, 电解质为Li⁺或Cs⁺时, H₂与CO的法拉第效率图

Figure 1 (Color online) Effect of cations on the electrochemical reduction of CO₂ over Ag^[36]. (a) pK_a of hydrolysis of hydrated Li⁺ and Cs⁺ inside the Helmholtz layer and in the bulk electrolyte; (b) distribution of pH and CO₂ concentration in the boundary layer and in the bulk electrolyte; (c) Faradaic efficient for CO and H₂ produced over Ag in Li⁺ and Cs⁺ electrolyte

图2 在水(实线)和[Emim][BF₄](虚线)中CO₂+2H⁺+2e⁻⇌CO+H₂O自由能变化示意图^[48]

Figure 2 A schematic of how the free energy of the system changes during the reaction $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ in water (solid line) or [Emim][BF₄] (dashed line)^[48]

解质, 电化学还原CO₂的主要产物是草酸. 而在相同体系下利用1-乙基-3-甲基咪唑双三氟甲基磺酰亚胺([Emim][Tf₂N])离子液体作为电解质, CO₂还原产物则

为CO, 表明离子液体的存在改变了反应途径. 大量文献报道咪唑类的阳离子较其他离子液体阳离子表现更高的CO₂还原制CO活性, 而阴离子对还原活性影响不大^[50,51]. Compton课题组^[51]在Ag电极上, 考察[Tf₂N]⁻为阴离子, 不同阳离子1-丁基-3-甲基咪唑([Bmim]⁺)、[Emim]⁺、1-丙基-3-甲基咪唑([Pmim]⁺)和1-丁基-1-甲基吡咯烷([Bmpyr]⁺)对CO₂还原性能的影响. 结果发现阳离子不同时, CO₂还原的起始电位不同, 其中[Bmim][Tf₂N]表现出最佳的CO₂还原生产CO的效果. 进一步以[Bmim]⁺为阳离子, 考察四氟硼酸阴离子([BF₄]⁻)、[Tf₂N]⁻和三(五氟乙基)三氟磷酸阴离子([FAP]⁻)对CO₂还原反应的影响, 结果发现阴离子的改变对CO₂还原反应的性能影响不大. 离子液体结合非贵金属作为电极还原CO₂制CO也是研究热点, 如Salehi-Khojin课题组^[52]利用N掺杂的碳纳米纤维和[Emim][BF₄]进行CO₂还原反应, 得到98%CO法拉第效率, 推测是[Emim]-CO₂中间体与碳纳米纤维中的还原性碳原子共同作用的结果. 同时Han课题组^[53]在H型电解池中利用不含金属的N和P共掺杂的碳凝胶作为工作电极, 在1-丁基-3-甲基咪唑六氟磷酸盐([Bmim][PF₆])中展现良好的CO₂还原性能,

该体系高达 143.6 mA/cm^2 的电流密度归功于离子液体与含N、P掺杂的碳材料的协同作用。

咪唑类离子液体具有良好的 CO_2 还原制CO反应活性,因此学者对咪唑类离子液体中 CO_2 还原制CO的机理进行深入研究. Brennecke课题组^[49]提出在Pb电极上, CO_2 会先得一个电子形成吸附态的 $\text{CO}_2^{\cdot-}$,当电解质中含 $[\text{Emim}][\text{Tf}_2\text{N}]$ 时, $[\text{Emim}]^+$ 也会吸附在电极表面,竞争电极表面的活性吸附位点,抑制 $\text{CO}_2^{\cdot-}$ 二聚反应,加速CO产物的形成(图3).此外, Masel课题组^[54]在 CO_2 还原过程中利用和频振动光谱表征技术(sum frequency generation, SFG),发现阴极表面存在 $[\text{Emim}]^+$ 单分子层,且电极表面的单分子层会与 CO_2 形成 $[\text{Emim}]\text{-CO}_2\text{-}[\text{BF}_4]$ 的复合中间态,大大降低生成CO的过电势.表明离子液体在电极表面形成单分子层的吸附行为是促进还原反应发生的主要原因^[55,56].除此之外也有研究表明,咪唑类离子液体在低浓度时性质如同表面活性剂,随浓度增加在电极表面阳离子的数目增加,当浓度增大到一定程度后,阳离子在电极表面铺满且通过静电相互作用等吸附溶液中的阴离子,促进了还原反应的发生. Dlott课题组^[57]利用非共振和频光谱表征技术,研究了在电极表面形成单分子层的咪唑类离子液体结构与 CO_2 还原过电势之间的关系.在一定的电势扫描范围内,Ar和 CO_2 气氛中在相近的电势下均出现非共振强度

峰,峰强度最小值的位置与 CO_2 起始还原电位一致,说明 CO_2 还原电势主要由吸附在电极表面的离子液体结构决定.

综上所述,咪唑类离子液体的阳离子对 CO_2 还原过程起主要作用,其中咪唑类离子液体较其他离子液体具有高的 CO_2 还原活性.可能与吸附在电极表面上的咪唑类离子液体的阳离子结构有关,从而影响了反应产物的选择性以及 CO_2 还原过电势^[58-63],但咪唑类离子液体的阳离子与 CO_2 作用生成CO的活性位点仍需进一步探究. Rosenthal课题组^[59]发现当1-丁基-2,3-二甲基咪唑四氟硼酸盐($[\text{Bmmim}][\text{BF}_4]$)为电解质,即 C_2 位被取代时,电化学还原 CO_2 的电流密度和法拉第效率相对于 $[\text{Bmim}][\text{BF}_4]$ 电解质均降低,认为咪唑类阳离子的 C_2 位为活性位点,促进 CO_2 还原形成CO. Dyson课题组^[64]在Ag电极表面研究系列的不同取代基咪唑类离子液体,发现当 C_2 位被甲基化时, CO_2 的还原活性未受到影响,而当咪唑的 C_4 和 C_5 位置被取代时, CO_2 还原活性明显降低,推测咪唑的 C_4 和 C_5 中的氢质子可稳定反应中间态,而 C_2 位则保持反应体系的高稳定性.虽然实验结果表明咪唑类离子液体作为电解质时,具有良好的 CO_2 还原活性,且利用原位表征技术观测到某些反应中间态,但其还原机理仍不明了. Nakamura课题组^[65]通过DFT计算模拟,提出了 CO_2 在 $[\text{Emim}][\text{BF}_4]$ 电解质中的反应路

图3 (网络版彩色)Pd电极上 CO_2 的电化学还原路径^[49]. (a) 不含 $[\text{Emim}][\text{Tf}_2\text{N}]$; (b), (c) 含 $[\text{Emim}][\text{Tf}_2\text{N}]$. (a) Absence of $[\text{Emim}][\text{Tf}_2\text{N}]$; (b), (c) presence of $[\text{Emim}][\text{Tf}_2\text{N}]$

径(图4)。咪唑环C₂位可活化CO₂分子,且C₂位上的氢作为质子源与CO₂结合形成[Emim-COOH]⁻过渡态,再经过质子/电子转移形成CO,而水本身作为复合催化剂为咪唑阳离子提供质子,保持咪唑阳离子的活性。总之,C₂位被取代的咪唑类离子液体促进CO₂还原的反应机理,仍需结合分子模拟和量化计算方法进一步深入研究。

2.2 CO₂电化学还原制HCOOH过程中离子液体电解质

电化学还原CO₂的产物除CO外,HCOOH也是常见的还原产物,且其商业应用价值更大,除了作为化工生产的反应原料外,还可作为储氢材料^[66],因此受到广泛关注。Compton课题组^[67]利用预氧化处理的Pt电极和[Emim][Tf₂N]电解质,在常温常压下可还原CO₂生成HCOOH。Hardacre课题组^[68]利用对CO₂具有化学吸收作用的功能化离子液体3-己基-14-烷基三氮唑季磷盐([P₆₆₆₁₄][124Triz])为电解质,在Ag电极表面上,低电势下获得了高达93%的HCOOH法拉第效率。而对CO₂具有物理吸收作用的3-己基-14-烷基季磷双三氟甲基磺酰亚胺盐([P₆₆₆₁₄][Tf₂N])⁺,则在高电势下还原CO₂生成CO。同时有研究者开发具有化学吸收CO₂的功能离子液体作为电解质,同样得到高法拉第效率的HCOOH产物^[69,70]。除贵金属外,Hu课题组^[71]将金属氧化物MoO₂负载在Pb电极上,在[Bmim][PF₆]为电解质体系中电化学还原CO₂,获得60%的HCOOH法拉第效率,其过电势仅为0.04 V。Fontecave课题组^[72]报道了一种用于CO₂还

原的多孔树突状纳米铜电极,在[Emim][BF₄]电解质中检测到HCOOH的法拉第效率为90%,且电流密度>10 mA/cm²,推测是CO₂在离子液体电解质中高溶解度与多孔树突状的Cu电极提供多活性位点的协同作用。Han课题组^[73]采用金属氧化物PbO₂电极,在1-苄基-3-甲基咪唑四氟硼酸盐([Bzmim][BF₄])电解质中,得到95.5%的HCOOH法拉第效率和40.8 mA/cm²的电流密度,还发现含F离子液体具有更好的CO₂还原性能。

为了获得更优的还原体系,学者对离子液体电解质中还原CO₂制HCOOH的机理进行了探究。Braunschweig课题组^[74]在Pt电极上,利用SFG和原位红外光谱手段,发现[Bmim][BF₄]在一定的电势扫描区域中出现的准可逆的氧化还原峰归因于咪唑阳离子的电子形成卡宾基团,在CO₂气氛中C₂位的卡宾基团会出现[Bmim]-COOH,因此提出CO₂还原生成HCOOH的机理图(图5)。此外利用拉曼光谱和DFT计算证明咪唑类阳离子的C₂位可形成卡宾基团,随后卡宾基团对CO₂中的C亲核攻击生成C₂位的羧酸盐,经质子转移最终形成HCOOH^[75-77]。除了阳离子对CO₂电化学还原的影响,阴离子的作用也引起人们的关注。Hardacre课题组^[68]提出超强碱阴离子[124Triz]⁻可通过化学作用和CO₂分子形成化学键,直线型CO₂分子被弯曲,生成[124Triz]-CO₂⁻中间物而后得质子/电子,在低电位下还原生成HCOO⁻,最终形成HCOOH产物,或发生深度还原生成4电子的还原产物甲醛(图6)。Zhang课题组^[70]利用DFT模拟计算,发现超强碱离子液体与CO₂之间存在的相互作用较其他常规离子液体的相互作用强,强的相互作

图4 [Emim][BF₄]电解质中CO₂反应机理图^[65]

Figure 4 Overall CO₂ reduction mechanism in [Emim][BF₄]^[65]

图 5 Pt电极[Bmim][BF₄]电解质中还生成CO和HCOOH的反应机理图^[74]

Figure 5 Overall reduction mechanism for the formation CO of and HCOOH at Pt/[Bmim][BF₄] electrode/electrolyte interfaces^[74]

图 6 不同CO₂饱和的离子液体在Ag电极表面的还原过程^[68]

Figure 6 Reduction process at Ag electrode in different ionic liquid saturated with CO₂ [68]

用导致CO₂的分子构型发生显著变化,活化O—C—O的键角由180°变为136°,键角远小于其他离子液体阴离子与CO₂的络合角度,因而在超强碱离子液体体系中获得更高的HCOOH电流密度和选择性.

2.3 CO₂电化学还原制CH₃OH等过程中离子液体电解质

目前,除了将 CO_2 还原制 CO 和 HCOOH 这些2电子产物,利用离子液体电解质在价格低廉的非贵金属电极上获得高法拉第效率和高电流密度的 CH_3OH 、 CH_4 和 CH_3COOH 等还原产物,也是当前的一个研究热点^[78-86]。Han课题组^[79]以Mo-Bi双金属硫化物纳米片为

阴极, 在[Bmim][BF₄]体系中CO₂还原反应, CH₃OH产物的法拉第效率可达71.2%, 同时发现随[Bmim][BF₄]浓度增加, CH₃OH的电流密度增大; 但浓度>0.5 mol/L时, CH₃OH的电流密度反而降低. 推测与离子液体的电导率有关, 随着电解质中离子数目增多, 电导率会增加, 但黏度也会增大, 使电导率有所下降, 因此低黏离子液体的设计尤为重要. Han课题组^[80]以[Bmim][BF₄]为电解质, 采用Pd₈₃Cu₁₇双金属气凝胶电极, 获得高达80%的CH₃OH法拉第效率, 且电流密度达31.8 mA/cm², 实验过程中还发现电解质中不含离子液体时, CO₂还原产物以H₂以及微量的HCOOH为主, 说明离子液体的加入可调控CO₂还原产物的选择性. 除甲醇产物外, Han课题组^[82]利用Zn-MOF作为催化剂和纯1-丁基-3-甲基咪唑高氯酸盐([Bmim][ClO₄])为电解质, 在低电势下(0.25 V)还原CO₂生成CH₄的法拉第效率达88.3%, 但采用四丁基四氟硼酸铵(TBABF₄)作为电解质时, CH₄法拉第效率极低. 尽管离子液体作为电解质, 可将CO₂高效深度还原生成CH₃OH、CH₄等产物, 但其相关机理研究极度匮乏, 将成为CO₂电化学还原领域中未来研究的难点和热点.

3 结论与展望

本文综述了碱金属盐和离子液体电解质对电化学还原 CO_2 制化学品的研究进展,系统分析了不同因素对其性能的影响规律及反应机理.分析表明,电化学还原 CO_2 的反应活性高度依赖于电极表面的局部环境,如电解质中碱金属阳离子的种类不同,相应的阳离子水解 $\text{p}K_{\text{a}}$ 也不同,会改变近电极表面的 pH ;且金属阳离子会在电极表面产生界面电场,稳定中间体以及促进 $\text{C}-\text{C}$ 耦联;当离子液体为电解质时,离子液体会吸附在电极表面形成单分子层,且离子液体与 CO_2 分子之间存在的相互作用力可降低生成 CO_2^- 的过电势,最终与电极协同作用而影响反应性能.对比两种电解质的影响可以发现,离子液体电解质作为新型介质和材料,在一些情况下,表现出较碱金属盐体系更高的 CO_2 电化学还原活性,表明离子液体在 CO_2 电化学还原领域具有优势和应用前景.围绕离子液体体系,未来重点开展如下研究:

(1) 探究离子液体电解质的结构与 CO_2 还原活性关系和反应机理.结合模拟计算和原位实验表征技术,深入认识离子液体结构与 CO_2 反应活性之间的还原规律;明确离子液体体系中的质子/电子的转移过程与催化材料的界面结构之间的协同作用机制.

(2) 开发 CO_2 电化学还

原生成多碳产物的离子液体电解质体系。设计可活化CO₂分子和促进反应中间态的C-C偶联的功能化离子液体电解质,以及与之匹配的还原性能优异的电极材料,特别是非贵金属还原体系,为CO₂电化学反应提供良好的反应环境,形成高效低能耗的CO₂还原合成多碳产物的离子液体电解质体系。(3)开展离子液体体系CO₂还原装置的流动传质及稳定性研究。研究不同结构的电化学还原装置对CO₂还原制化学品性能的影响,优化电解池内部结构、电极结构、电解液流动类型等,为CO₂电化学还原提供良好的反应场所。同时,离子液

体的稳定性对长周期运行至关重要,开发结构稳定的离子液体也是研究重点。

总之,离子液体强化的电解质CO₂电化学还原体系的转化利用及放大研究技术,是实现碳减排和转化利用的重要途径,有望形成新一代的CO₂利用的变革性技术。尽管目前大规模的CO₂电化学还原制化学品的研究还处于基础研究和工业化起步阶段,但可以预见未来该项技术的突破将会有效缓解化石能源的紧缺及大气环境的恶化等问题,对人类社会的可持续发展具有重要的意义。

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补充材料

表S1 离子液体电解质对CO₂还原活性的影响

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Summary for “CO₂电化学还原过程中电解质研究现状及趋势”

Research status and trend of electrolytes in the CO₂ electrochemical reduction

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The concentration of CO₂ in the atmosphere increases with utilizing fossil energy, which caused serious environmental problems. Owing to the advantage of using renewable electricity, the issue of carbon recycling and energy recovery based on the electrochemical CO₂ reduction reaction (CO₂RR) presents a potentially sustainable way to transform CO₂ into a variety of valuable products, such as carbon monoxide (CO), methanol (CH₃OH), formic acid (HCOOH/HCOO⁻), and so on. The challenges of CO₂RR mainly include high overpotential, low current density and low Faraday efficiency (FE). Therefore, the development of new electrochemical reduction systems to reduce overpotential and improve reaction selectivity is the research hotspot in CO₂RR.

The selection of the electrolyte is very important to design efficient electrochemical reduction systems, which provides the reaction environment, transports ions and serves a conductive medium in CO₂RR system. Under the same condition, the species, concentration, and pH of electrolytes influence the local reaction environment, the current density and the selectivity of products. So far, various electrolytes, such as alkali metal and ionic liquid electrolytes have been applied to enhance the performance of CO₂RR. Therefore, in comprehensive understanding of the electrolyte effects on CO₂RR is crucial in selecting proper electrolytes for the reduction of CO₂ to desired products.

This paper mainly reviews the recent processes in the alkali metal and ionic liquid electrolytes, and summarizes their effects in CO₂RR as well. Firstly, we summarize the product distribution and current density of CO₂RR in the different alkali metal aqueous. Alkali metal aqueous is the most common solvent for CO₂RR, because alkali metal aqueous are widely available at low cost, relatively easy to prepare, and store safely. Many studies reported that alkali metal aqueous effects CO₂RR current density and product distribution. The effects of metal aqueous on the CO₂RR based on preferential hydrolysis of hydrated cations near the cathode surface, which to buffer the electrolyte near the electrode surface, offsetting the polarization losses caused by concentration gradient. At the same time, hydrated alkali metal cations in the outer Helmholtz plane can create a dipole field, which can stabilize the adsorption the intermediates to enhance the selectivity of the CO₂RR on the intrinsic activity.

Secondly, ionic liquids as electrolytes have also attracted extensive interest due to their high electrical conductivity, high CO₂ adsorption capacity, and high selectivity. Because the ionic liquid can be adsorption on the electrode surface to reduce the overpotential and change the reaction microenvironment. Using different ionic liquid electrolytes can promote CO₂ electroreduction to different products, such as CO, HCOO⁻/HCOOH, CH₃OH and so on, especially in the performance of production selectively. Although important progress has been made in CO₂RR with ionic liquid electrolyte, the mechanism of CO₂RR to C₂₊ products is unclear, especially the interaction between the liquid and the electrode surface. Finally, we briefly prospect the future research priorities and directions of CO₂RR systems in ionic liquid electrolyte.

CO₂, electrochemical reduction, alkali metal aqueous, ionic liquid, reaction mechanism

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