

基于堆栈电解池的纳米 SnO₂ 电催化 CO₂ 还原试验

魏书洲^{1,2,3}, 谭舒婷⁴, 熊卓⁴, 徐祖伟⁴, 赵永椿⁴, 张军营⁴

(1. 国能三河发电有限责任公司, 河北 廊坊 065201; 2. 国家能源煤基能源碳捕集利用与封存技术研发中心, 河北 廊坊 065201; 3. 河北省燃煤电站污染防治技术创新中心, 河北 廊坊 065201; 4. 华中科技大学 煤燃烧与低碳利用全国重点实验室, 湖北 武汉 430074)

摘要: 利用新能源电能电催化还原二氧化碳(CO₂)技术能在减排降碳过程将CO₂转化为增值化学品,有广阔应用前景,在多种还原产物中,甲酸(HCOOH)易储存和运输,储氢密度高,应用前景好。氧化锡(SnO₂)电催化材料成本低、毒性小,且SnO₂用于电催化还原CO₂制HCOOH选择性高。而在电催化还原的工业化中,合理的电解池结构有重要意义。为探究更合理的电解池结构,提出一种自制的多层堆栈式电解池,将通过火焰喷雾热解方法制备的SnO₂纳米颗粒作为电催化剂,进行电催化还原CO₂研究。探究电解池的阴极-阳极间距、电解液流速、电解液浓度及电极堆栈数目等参数对电催化性能影响。试验结果显示:阴极-阳极距离越小,电能损耗越少,电催化还原CO₂性能更佳;电解液的流速对催化剂还原性能无明显影响,但过大的流速使反应的电流密度产生大的波动;在电解液浓度小于1 mol/L时,催化剂对HCOOH的选择性随着电解液浓度增加而增加,而在电解液浓度大于1 mol/L时,各产物的选择性趋于稳定;电极堆栈排放时,电流密度略下降,但整体法拉第效率和HCOOH的法拉第效率均所提高,并对析氢反应有较明显抑制作用。使用堆栈电解池可减小电荷转移电阻及扩散电阻。对于该堆栈电解池,在阴极-阳极间距10 mm、施加电位-1.2 V vs. RHE、KHCO₃浓度1 mol/L下,SnO₂在堆栈条件对HCOOH的法拉第效率达37.53%,且总的法拉第效率达75.83%。结果表明:使用堆栈电解池可提升催化剂催化性能,提升目标产物的选择性。

关键词: 电催化;堆栈电解池;新能源;CO₂;还原

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Experimental study of electrocatalytic CO₂ reduction by nano-SnO₂ based on stacked electrolytic reactor

WEI Shuzhou^{1,2,3}, TAN Shuting⁴, XIONG Zhuo⁴, XU Zuwei⁴, ZHAO Yongchun⁴, ZHANG Junying⁴

(1. Sanhe Power Generation Co., Ltd., Langfang 065201, China; 2. Utilization and Storage (CCUS) Technology for Coal-based Energy, National Energy Research and Development Center of Carbon Capture, Langfang 065201; 3. Hebei Province Coal-fired Power Station Pollution Prevention and Control Technology Innovation Center, Langfang 065201, China; 4. State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430000, China)

Abstract: The electrocatalytic reduction of carbon dioxide (CO₂) using new energy and electrical energy can convert CO₂ into value-added chemicals while reducing carbon emissions, which has broad application prospects. Among the various reduction products, formic acid (HCOOH) is easy to store and transport, with a high storage density of hydrogen. Tin oxide (SnO₂) electrocatalytic materials are low-cost and less toxic, while SnO₂ is highly selective for HCOOH when used for electrocatalytic reduction of CO₂. In the industrialization of electrocatalytic reduction, a reasonable electrolytic reactor structure is of great significance. To explore a more reasonable electrolytic reactor structure, this paper proposes a homemade multilayer stacked electrolytic reactor, in which SnO₂ nanoparticles prepared by flame spray pyrolysis method are used as electrocatalysts for electrocatalytic reduction of CO₂. The effects of parameters such as cathode-anode

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作者简介:魏书洲(1981—),男,湖北十堰人,高级工程师,博士.E-mail: shuzhou.wei@chnenergy.com.cn

通讯作者:张军营(1963—),男,山西平陆人,教授,博士.E-mail: jyzhang@hust.edu.cn

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spacing, electrolyte flow rate, electrolyte concentration and the number of electrode stacks on the electrocatalytic performance of the electrolytic cell were investigated. The experimental results show that: the closer the cathode-anode distance is, the lower the electrical energy loss is, and the catalyst has better catalytic performance; the flow rate of the electrolyte has no significant effect on the reduction performance of the catalyst, but when the flow rate is too fast, the current density of the reaction produces a more drastic fluctuation. When the electrolyte concentration was less than 1 mol/L, the selectivity of the catalyst for HCOOH increased with the increase of the electrolyte concentration, whereas the selectivity of the catalyst for each product stabilized at the electrolyte concentration of more than 1 mol/L. The current density decreased slightly when the electrodes were placed in stacks, but the overall Faraday efficiency and the Faraday efficiency of HCOOH both increased, and the hydrogen precipitation reaction was suppressed more significantly. The charge transfer resistance and diffusion resistance were reduced when using a stack electrolytic reactor. The optimum Faraday efficiency for HCOOH of SnO₂ under stack conditions reaches 37.53% and the total Faraday efficiency reaches 75.83% with the cathode-anode spacing of 10 mm, the applied potential of -1.2 V vs. RHE, and the KHCO₃ concentration of 1 mol/L. The results indicate that the catalytic performance of the catalyst and the selectivity of the target products can be enhanced by using a stacked electrolytic reactor.

Key words: electrochemistry; stack reactors; renewable energy; carbon dioxide; reduction

0 引言

随着社会经济快速发展,化石燃料大量消耗造成 CO₂ 的过度排放,引发了环境污染、温室效应、冰川融化等一系列问题。自工业革命开始以来大气中 CO₂ 浓度增幅已超 50%,严重破坏了自然碳平衡^[1]。为遏制气候变暖的加剧,碳捕集、利用与封存(Carbon Capture, Utilization and Storage, CCUS)技术受各国广泛关注^[2-6]。在酶催化^[7]、光催化^[8-10]、热催化^[11-13]和电催化^[14]等 CO₂ 利用技术中,电催化还原 CO₂ 被认为是最具吸引力和环境最友好的方式之一。电催化还原 CO₂ 利用风能、太阳能等可再生能源作为驱动将 CO₂ 转化为清洁碳氢燃料及增值化学品,是实现 CO₂ 高效转化和利用的有效途径。在某些情况下^[15-17],电催化可达净零 CO₂ 排放的理想条件。此外,电催化还原 CO₂ 技术的放大比光化学和热化学更简单^[18-19]。

目前电催化还原 CO₂ 研究主要集中在催化剂材料研发^[20-22]、电解液影响的探究^[23-24]上,但电解池的结构通常会一定程度影响反应的进行。电解池构型及其操作条件在较大程度决定了电极附近局部反应环境,调变催化性能^[25-27]。因此电解池的结构设计与优化对于提高反应效率、强化产物选择有重要意义,尤其是在未来工业化中,合理的电解池结构很重要。堆栈电极在燃料电池中已有相关报道,杨俏^[28]构建并研究紧凑堆栈生物电化学系统;ZHENG 等^[29]研究固体氧化物电解池(Solid Oxide Electrolytic Battery, SOEC)堆中电池、空气电极接触和氢电极接触的定量电化学贡献,探究电池、氢电极接触和空气电极接触的欧姆电阻;HEMMATIFAR 等^[30]展示了一种能给有效补集和释放 CO₂ 的双极细胞结构电化学介导 DA 系统。但堆栈装置在电催

化中研究较少。

笔者设计了一种堆栈电解池,用火焰喷雾热解法合成了 SnO₂ 作为电催化剂,研究堆栈电解池中电催化还原 CO₂ 的性能,为电催化还原 CO₂ 的的电解池设计与优化提供有益的参考。

1 试验

1.1 电极的制备与表征

1.1.1 SnO₂ 纳米颗粒的制备

通过火焰喷雾热解方法(Flame spray pyrolysis, FSP)制备 SnO₂ 纳米颗粒。将体积比 4:1 的无水乙醇和乙酸配制成溶剂,用有机金属盐 2-乙基己酸亚锡作为 Sn 源。然后将一定量 2-乙基己酸亚锡溶解在溶剂中,保持 2-乙基己酸亚锡的物质的量浓度 0.4 mol/L。将配制的前驱体溶液超声处理 5 min、磁力搅拌 10 min 以保证前驱体溶液各组分混合均匀。然后注射泵,通过反应器内毛细管,以 3 mL/min 的恒定进料速率,用 5 mL/min 的 O₂ 将前体溶液分散形成喷雾。前驱体液滴蒸发和燃烧后,借助真空泵将纳米粉末收集在玻璃微纤维过滤器上。

1.1.2 试验方法与计算

试验均在堆栈电解池(图 1)中用三电极体系进行,堆栈电解池为一体式结构,阴极阳极及参考电极被置于同一腔室内。5 个电极孔间隔分别为 10 mm。制备的碳纸电极(2.5×2.5 cm²)为工作电极,由玻碳电极夹固定置于反应腔中,铂片电极(2.5×2.5 cm²)为对电极,Ag/AgCl(sat. KCl)电极为参比电极。

电解液用 1 mol/L KHCO₃(pH=9.2),在稳流池中通入 20 SCCM(Standard cubic centimeter per minute)CO₂,CO₂ 自稳流池中出来后又作为吹扫气通入电解池内,将气体产物带进气相色谱检测。电解

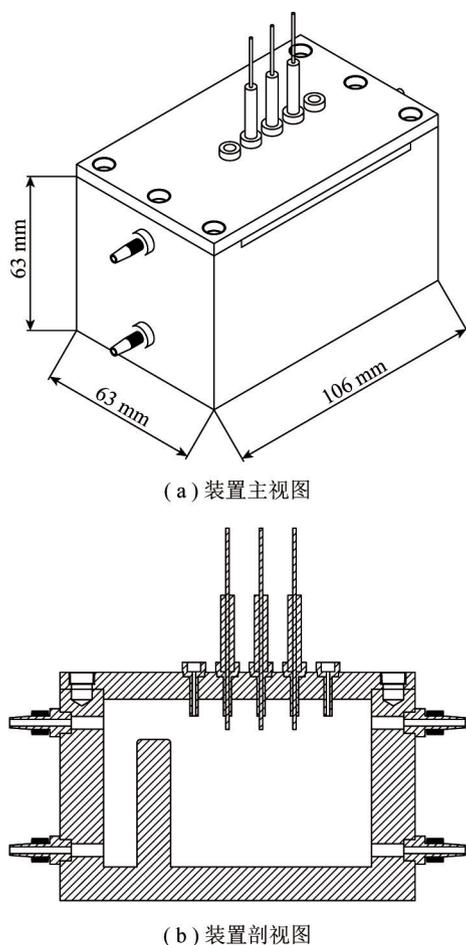


图1 堆栈装置示意

Fig.1 Diagram of stack reactor

液流速由蠕动泵控制,在稳流池中溶解 CO₂后进入电解池,参与反应后由自溢流池流出电解池进入稳流池吸收 CO₂,完成电解液的循环。

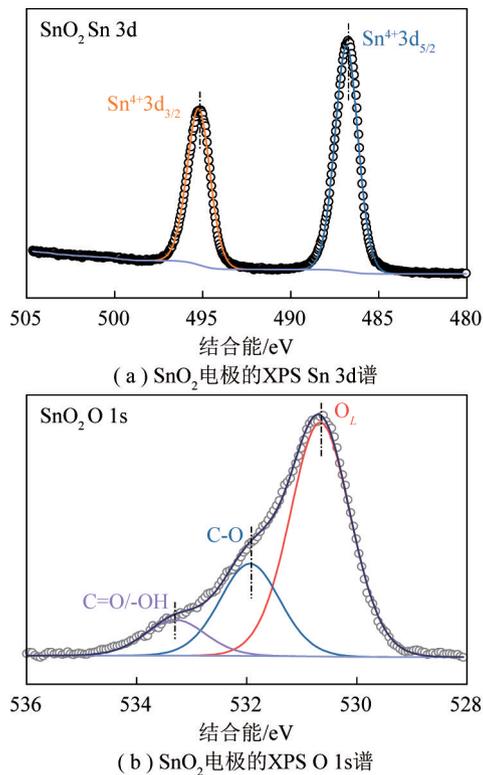
反应开始前,通入 CO₂ 30 min,得到 CO₂的饱和溶液。电解时间为 2 h,试验中所需电能由 CHI660D 电化学工作站提供,气相产物主要使用气相色谱仪 (Gas Chromatograph, GC) 检测。液相产物由 400 MHz 液相核磁共振谱仪 (Bruker AV400) 测试分析。

2 试验结果与讨论

2.1 催化剂表征

SnO₂的 XPS 测试结果如图 2 所示。由 Sn 2d 图谱(图 2(a))可知,主峰分别以 495.4 和 486.9 eV 为中心,二者价态相同,分别属于 Sn⁴⁺的 Sn 3d_{3/2}和 Sn 3d_{5/2}。O 1s 谱显示出一个不对称峰,由 3 个结合能分别以 530.7、531.7 和 533.4 eV 为中心的峰(图 2(b))。以 530.7 eV 为中心的峰对应于与 Sn 原子结合的表面晶格氧,以 531.7 eV 为中心的峰归因于表面吸附的氧,533.4 eV 为中心的峰则为其他

弱结合氧物种(OH⁻)。

图2 SnO₂的 XPS 图谱Fig.2 XPS spectrum of SnO₂

由 SEM 图谱(图 3(a))可知 SnO₂呈聚集状态的微球,颗粒大小不均一,约在 10~20 nm。利用高倍透射电镜图像进一步显示 SnO₂纳米颗粒的微观特征,纳米颗粒显示出约 20~40 nm 的类似多边形晶体结构。SnO₂的 HRTEM 及 XRD(图 3(b)和图 3(c))图中可观察到明显晶格条纹和较好的 SnO₂衍射峰,说明 SnO₂结晶较好。

2.2 堆栈电解池中 CO₂电催化还原性能

利用恒电位电解法在电解池上对 SnO₂催化剂进行电化学还原 CO₂试验,探讨堆栈电解池阴极与阳极之间最佳距离、电解液流速、电解液浓度及两组堆栈电极和单组电极等因素对电化学还原 CO₂特性影响规律。

2.2.1 阴极-阳极距离

研究阴极-阳极之间距离对电化学还原 CO₂性能影响,分别在阴极-阳极距离 10、20、30、40 mm 四种时,测试催化剂电催化还原 CO₂的性能。此时电解液流速 15 mL/min,电解液使用 1.0 mol/L 的 KHCO₃。

测试结果如图 4 所示,从线性扫描伏安测试 (Linear Sweep Voltammetry, LSV) 图可知 4 种情况下,电流密度都随着电位的负移而增大,原因是更负

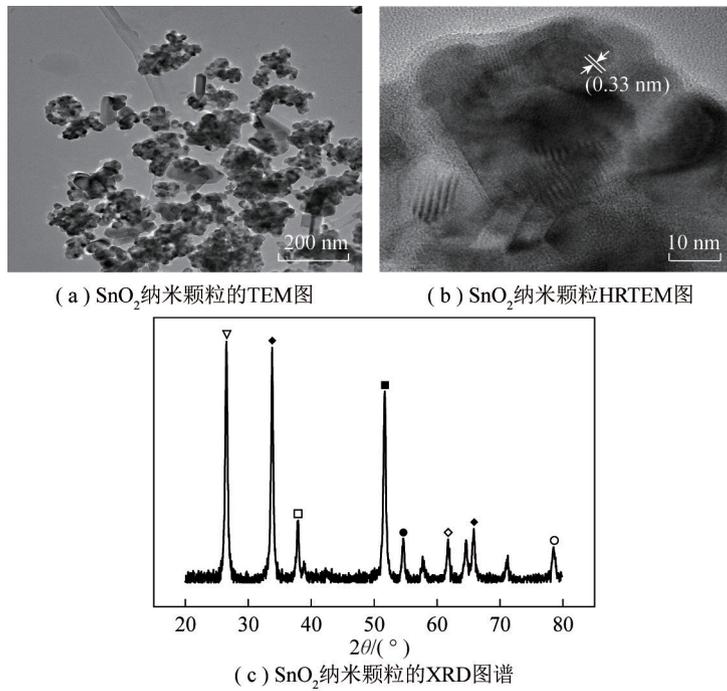
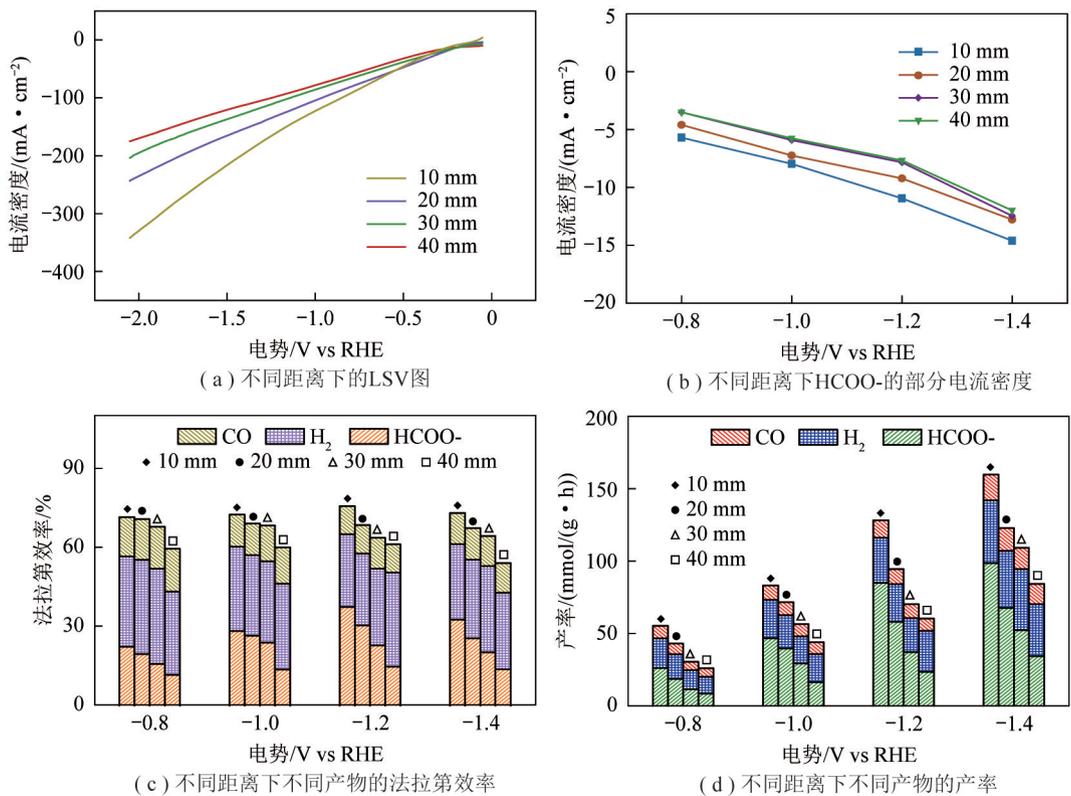
图3 SnO₂纳米颗粒的表征图谱Fig.3 Characterization of SnO₂ nanoparticles

图4 阴极-阳极不同距离的电化学表征

Fig.4 Electrochemical characterization of different cathode-anode distances

的电位提供更大的反应驱动力。不同间隔距离下,反应的起始电位差距小。相同电位下,随着距离增大,电极的电流密度逐渐减小,距离10 mm时,有最大电流密度。HCOO⁻的部分电流密度图显示,在相

同还原电位下,距离10 mm时,HCOO⁻有最大部分电流密度。图4(c)显示SnO₂的产物分布,4种情况下检测到还原产物均仅CO、H₂、HCOO⁻,在-1.2 V vs. RHE时,阴极阳极间距10 mm的电极对HCOO⁻

有最大法拉第效率 37.53%,此时,SnO₂对氢气的选择性为 27.63%,对 CO 的选择性为 10.68%,此时电流密度分别为 $(10.96 \pm 0.7) \text{ mA/cm}^2$ 。CO 的法拉第效率也呈现先降低后升高趋势,说明作为 CO₂还原产物,CO 与 HCOO⁻也存在着竞争关系。由不同距离下不同产物的产率图(图 4(d))可知不同产物的产率随阴极阳极距离减小而增加,距离 10 mm 时,HCOO⁻、CO 及 H₂总的产率有最大值。说明在研究范围内,距离越近,电能损耗越少,电催化还原 CO₂性能越高,对 HCOO⁻的选择性也越高。因此后续试验中选择阴极阳极距离 10 mm。

2.2.2 电解液流速

在阴极-阳极距离 10mm 时,探究电解液流速对电催化还原 CO₂性能影响,选择电解液流速分别为 15、25、35、45 mL/min 进行试验,此时电解液浓度 1 mol/L。各流速下 LSV 图及产物的法拉第效率及产率如图 5(a)、5(b)、5(c)所示,不同电解液流速下,催化剂还原 CO₂的性能相差小。不同流速下在 -1.4 V vs. RHE 时的 i-t 图如图 5(d~g)所示,随流速增加,电流密度相差小,但大的电解液流速会导致电流不稳定,波动大。因此在后续试验中选择相对稳定的流速 15 mL/min 进行试验。

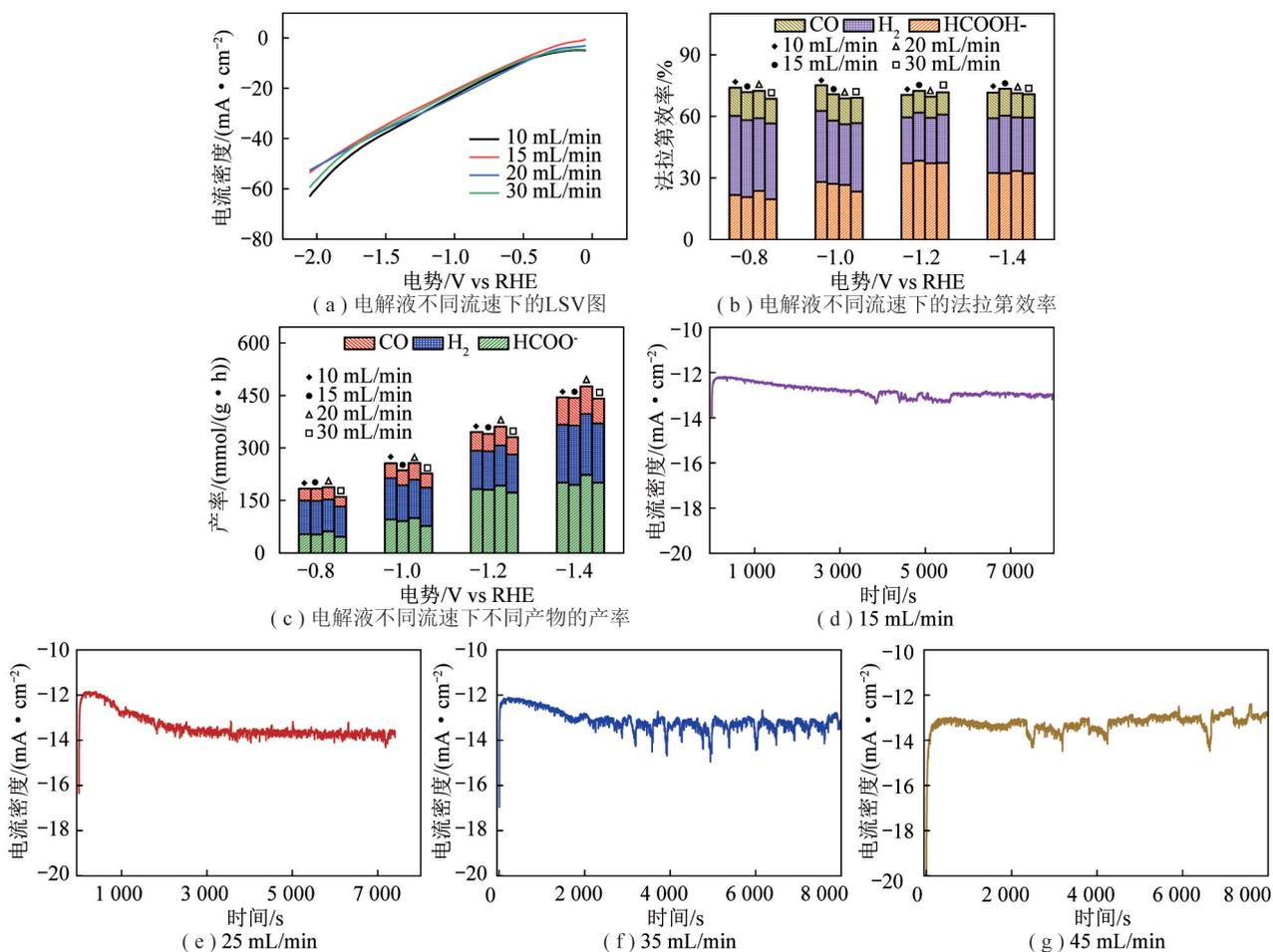


图5 电解液不同流速下电化学表征

Fig.5 Electrochemical characterization of electrolyte at different flow rates

2.2.3 电解液浓度

在阴极-阳极距离 10 mm, 电解液流速 15 mL/min 时, 探究不同电解液浓度对 SnO₂ 电催化还原 CO₂ 性能影响, 分别测试 KHCO₃ 浓度 0.1、0.5、1.0、1.5 及 2 mol/L 时的 LSV 曲线, 结果如图 6(a)

所示。相同还原电位下, 随电解液浓度增加, 电流密度呈递增趋势, 在 1.5 mol/L 后, 电流密度不再随电解液浓度升高继续增加。在电解液浓度分别为 0.1、0.5、1.0、1.5 mol/L 条件测试 SnO₂ 电化学还原 CO₂ 的性能, 不同浓度下法拉第效率如图 6(b) 所示。

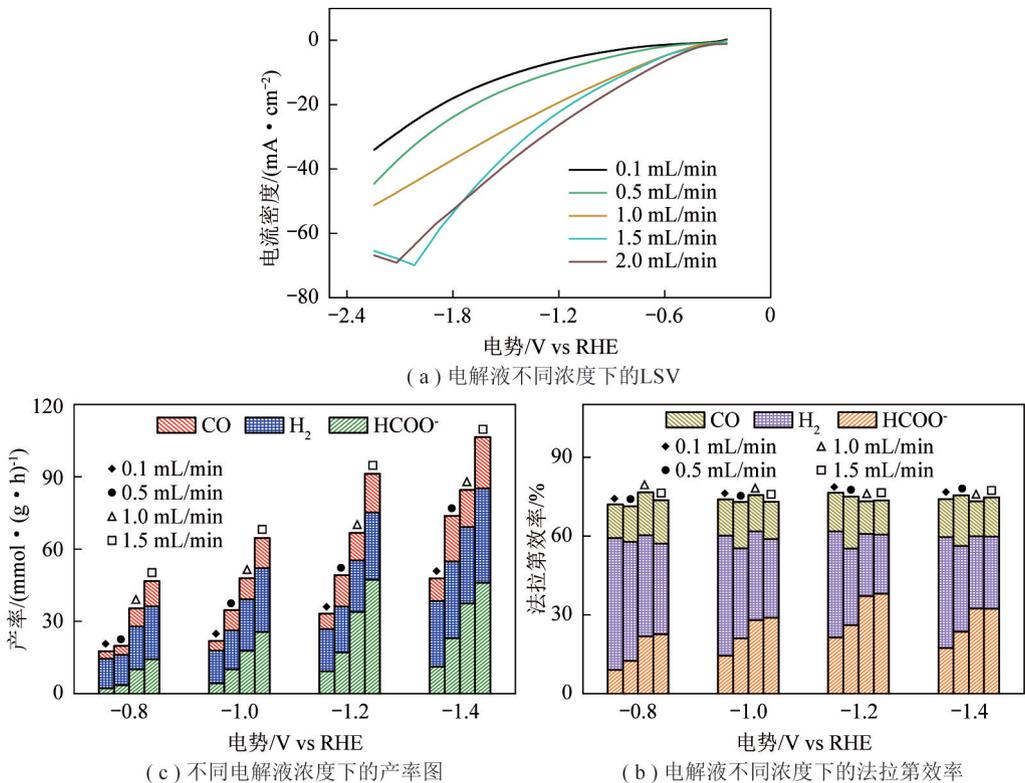


图6 不同电解液浓度下电化学表征

Fig.6 Electrochemical characterization of different electrolyte concentrations

在电解液浓度低时, SnO_2 对 H_2 的选择性高, 随电解液浓度增加, 溶液存在更多 HCO_3^- , 催化剂对 HCOO^- 的选择性提高, 对 H_2 的选择性降低, 表明提高电解液浓度对抑制析氢反应效果明显。但在浓度达 1 mol/L 后继续增加时, 催化剂对各产物的法拉第效率不再发生显著变化。由此推断, 在研究范围内, SnO_2 在该电解池中最佳电解液浓度 1 mol/L 。

2.2.4 堆栈电极

在前面试验中, 已测试出在阴极-阳极距离 10 mm 时, SnO_2 电极有最佳 CO_2RR 性能。接下来测试在有两组间隔为 10 mm 的堆栈电极时, 电解液流速 15 mL/min 、电解液浓度 1 mol/L 时, 催化剂电化学还原 CO_2 还原性能, 由图 7(a) 可知相同电位下, 堆栈电极的电流密度稍小于单组电极的电流密度。由图 7(b) 可知堆栈电极的法拉第效率相较于单组电极略提升, 在 -1.2 V vs. RHE 时, SnO_2 对 HCOO^- 的选择性由单组的 37.53% 升至 40.81% , 对氢气的法拉第效率则由 27.63% 降至 26.91% , SnO_2 的总法拉第效率也由 75.83% 升至 76.21% 。原因是增加 1 组电极后, 电解液扩散电阻进一步减小, 进一步提高电能利用效率。通过改变电流密度也可调节氢气析出量。表明堆栈电极对析氢作用能起一定抑制作用。由图 7(c) 可知, 无论单组电极还是堆栈电极, 均可

长期稳定工作。由图 7(d) 可知增加 1 组电极后, 催化剂产率增加, -1.4 V vs. RHE 时 HCOO^- 的最大产率由 $98.59 \text{ mmol}/(\text{g} \cdot \text{h})$ 增至 $102.69 \text{ mmol}/(\text{g} \cdot \text{h})$ 。可见堆栈电极可提高催化剂利用效率, 在等量能源输入下产生更多目标产物。

2.3 电极电化学表征

通过双电层电容法对 SnO_2 电极的电化学活性面积 (Electroactive surface area, ESCA) 进行表征。结果如图 8 所示, 可知堆栈电极的双电层电容略小于单组电极的 2 倍。

对电极进行电化学阻抗 (Electrochemical Impedance Spectroscopy, EIS) 测试, 频率 $100 \text{ kHz} \sim 10 \text{ MHz}$, 结果如图 9 所示, 等效电路图中 R_s 为溶液电阻, CPE 为容抗, R_{ct} 为充放电电阻, W_0 为扩散阻抗。可见随距离增加, 在高频区半圆直径变化小, 表明在 4 种条件电荷转移电阻差别小, 而当距离增大时, 低频区域斜率变大, 表明电荷转移电阻随距离增加逐渐增大。原因是在电解液之中, 质子由阳极向阴极扩散路径增加。由此引起扩散电阻显著增大。堆栈电极相较于单组电极而言, 高频区域半径小, 表明堆栈电极有相对更小电荷转移电阻, 原因是两阴极电极为并联关系。此外堆栈电极中扩散电极也有所减小。

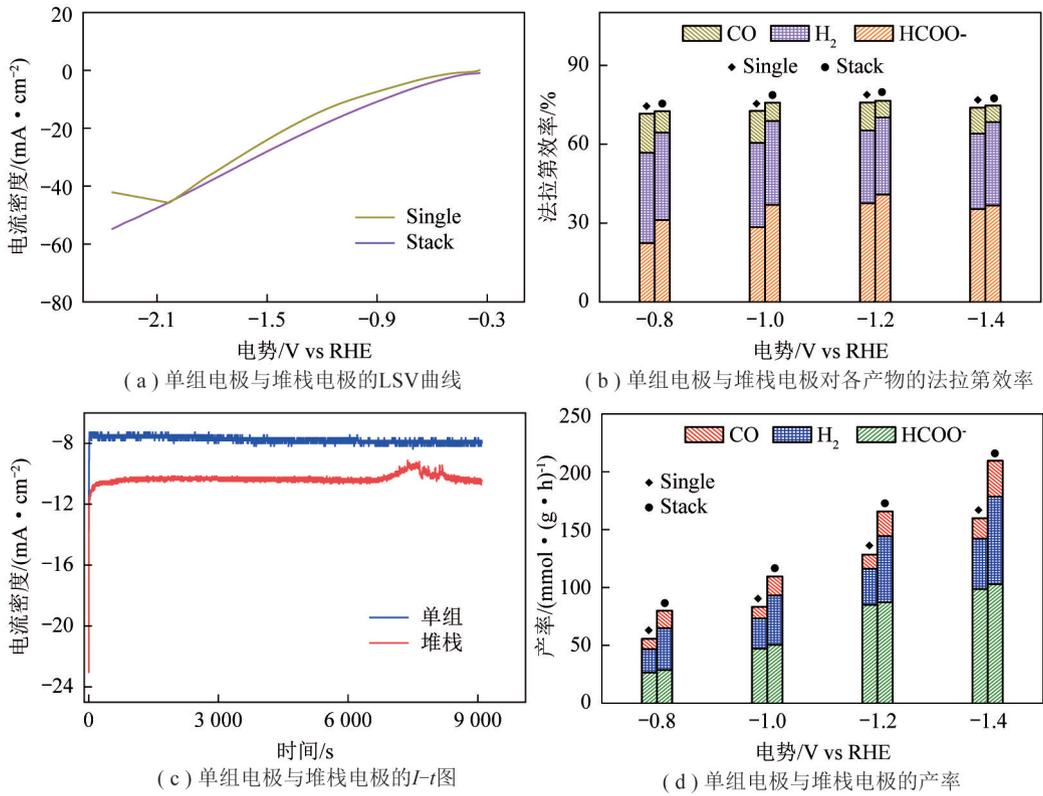


图 7 单组电极与堆栈电极的电化学表征

Fig.7 Electrochemical characterization of single- and stack electrodes

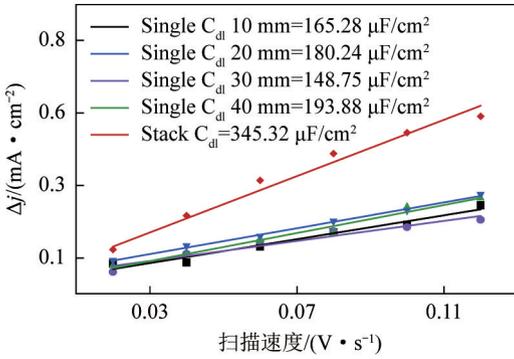


图 8 单组电极和堆栈电极的电化学活性面积

Fig.8 Characterization of electrochemically active area of single- and stacked electrodes

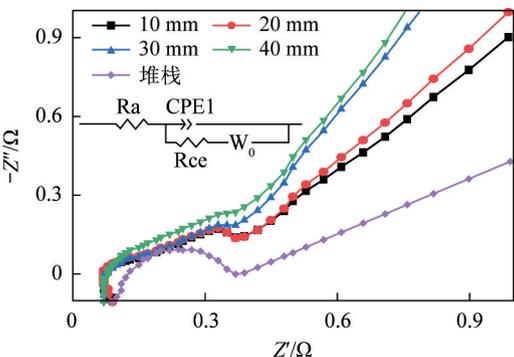


图 9 阴极-阳极不同距离及堆栈电极的电化学阻抗表征

Fig.9 Electrochemical impedance characterization of cathode-anode with different distances and stacked electrodes

3 结 论

1) 提出一种多层堆栈式电解池,制备 SnO₂ 纳米颗粒作为电催化剂,电流密度随距离增大而降低,抑制析氢的能力下降,HCOO⁻ 的法拉第效率下降。

2) 距离 10 mm 时,在 -1.2 V vs. RHE 对 HCOO⁻ 有最优的法拉第效率 37.53%,总法拉第效率最高为 75.83%。

3) 电解液流速对催化剂还原性能没明显影响,但过大的流速使反应的电流密度波动大;电解液浓度升高对增强 HCOO⁻ 选择性及抑制析氢反应效果显著,浓度超过 1 mol/L 后,催化剂对各产物的选择性趋于稳定;

4) 评估了堆栈电极对电催化性能影响,布置 2 组间距 10 mm 的电极时,整体法拉第效率和 HCOO⁻ 法拉第效率提高,为电催化还原 CO₂ 的电解池设计与优化提供一种有益参考。

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