第 27 卷 第 1 期
2021 年 2 月

电化学
JOURNAL OF ELECTROCHEMISTRY

Vol. 27 No. 1
Feb. 2021

【Review】 **DOI**: 10.13208/j.electrochem.200802 **Http**://electrochem.xmu.edu.cn

钛基氧化铱电极电沉积制备技术研究进展

吴丹丹,吴 旭*

(华中科技大学环境科学与工程学院,湖北 武汉 430074)

摘要: 钛基氧化铱电极作为 DSA(dimension stable anode)中的典型电极,广泛应用于各个领域。目前工业生产的钛基氧化铱电极主要由传统热分解法制备,存在成本高昂,工艺繁琐,依赖人工劳动,无法大规模生产等问题,十分有必要探索开发新的制备技术。本文从沉积液配方、基底材料的选择及处理、电沉积方式以及沉积时间等方面系统地讨论了氧化铱电沉积制备技术的研究进展,包括作者课题组所作的一些工作及成果;分析了钛基氧化铱电极电沉积制备技术目前所面临的挑战,并给出一定建议;阐述了其应用前景,展望了其未来发展方向,希望更多的科研人员能投入到相关研究中。

关键词: 钛基氧化铱电极;电沉积;工业应用

1 引 言

铱系涂层钛阳极具有低的析氧电位、大电流密度承载能力(> 100 A·dm^{-2})、优良的催化活性,卓越的电耐久性等优点[1-3],自开发以来,广泛应用于电解水、阴极保护、电镀、有色金属提取、水处理、蚀刻液回收等领域。1973 年,Bianchi 取得 IrO_2/Ta_2O_5 涂层电极专利权,自此,奠定了热分解法制备铱钽涂层钛电极的核心地位[4]。目前研究的钛基氧化铱电极的制备方法有热分解法、溶胶-凝胶法、磁控溅射法、电沉积、热解喷涂、MOCVD(金属有机化学气相沉积)等,对各种方法的介绍及其特点归纳总结见表 1。

随着不溶性钛阳极市场需求不断扩大,国家对工业体系升级的重视,传统的热分解法已经不能满足工业生产要求,顺应工业时代发展。溶胶-凝胶法、磁控溅射沉积法等虽然能制备纳米级涂层,且氧化铱成膜效果好,但由于其设备复杂,工艺过程要求严苛,未有相关明确切合研究,无法为实际工业中大型铱系涂层钛电极制备提供相关理论依据,可操作性较小。电沉积法由于其本身具有制备条件温和,机械化程度高,可操作性强等特点,十分契合于实际工业体系铱系涂层钛电极的制备。

2 研究进展

近年来关于氧化铱电极的研究主要分为三个方面:pH 传感微电极、多聚物膜电极以及 DSA 阳极的电沉积制备技术。如图 1 所示,列举了部分氧化铱电沉积技术在这方面的研究应用情况[9,10]。其中,pH 传感微电极多以铂为基底进行氧化铱的电沉积,其沉积体系除传统三电极、两电极体系外,还有一种新型的模板化电化学沉积工艺,Jin Hu[11]等利用该法制备了纳米结构 IrO_x 薄膜。pH 传感微电极主要利用氧化铱优秀的质子结合能力,以及灵敏的显色反应,从而监测溶液 pH 值。Elisabet Prata-Alfonso[10]就其作为 pH 微传感器的灵敏度进行了研究,结果表明其对于 pH 值在 3 ~ 11 的溶液,反馈可达 72.9 mV·pH^{-1}。多聚物膜电极作为水电解设备的核心电极组件,通常以 CP(carbon paper)为基底进行氧化铱的电沉积。Byung-Seok Lee[9]通过改变沉积电压及沉积时间控制 CP 上氧化铱的沉积量,研究表明,当 IrO_2/CP 电极上 IrO_2

引用格式: Wu D D, Wu X. Research progress in electrodeposition technology of titanium-based iridium oxide electrode. *J. Electrochem.*, 2021, 27(1): 35-44.

收稿日期: 2020-08-14,修订日期: 2020-08-27. * 通讯作者, Tel: (86)18571590300, E-mail: Profxuwu@hust.edu.cn

表 1 钛基氧化铱电极制备技术简介及其特点[1,2,5-8]

Table 1 Introduction to the preparation technology of iridium oxide titanium electrode and its characteristics[1,2,5-8]

Technology	Introduction	Characteristics
Thermal decomposition	Iridium-containing coating solution is coated on the pretreated titanium substrate by brushing, and then cementation so repeated.	Simple and widely applicated Process is cumbersome, and need manual labour
Sol-gel method	The compound containing high chemically active components is solidified by solution, sol, gel, and then heat-treated to form oxide or other compound solids.	Scale is uniform and crystal grains are fine Preparation process is complicated and raw materials are expensive and harmful.
Magnetron sputtering	Bombarding the target surface with energetic particles in a vacuum to deposit the bombarded particles on the substrate.	Deposition speed is fast, no impurities remain; Process and devices are complicated and high cost.
Laser pulse deposition	A laser is used to bombard an object, and then the bombarded material is deposited on a certain substrate to obtain a thin film or a deposited layer.	Deposition rate is high. The large area can be deposited Film formation is not suitable, and high cost
Electrodeposition	Iridium-containing metal salt ion undergoes oxidation or reduction reaction to deposit on the titanium substrate.	Coating has high cleanliness and homogeneity, high degree of mechanization, and process flow is simple.

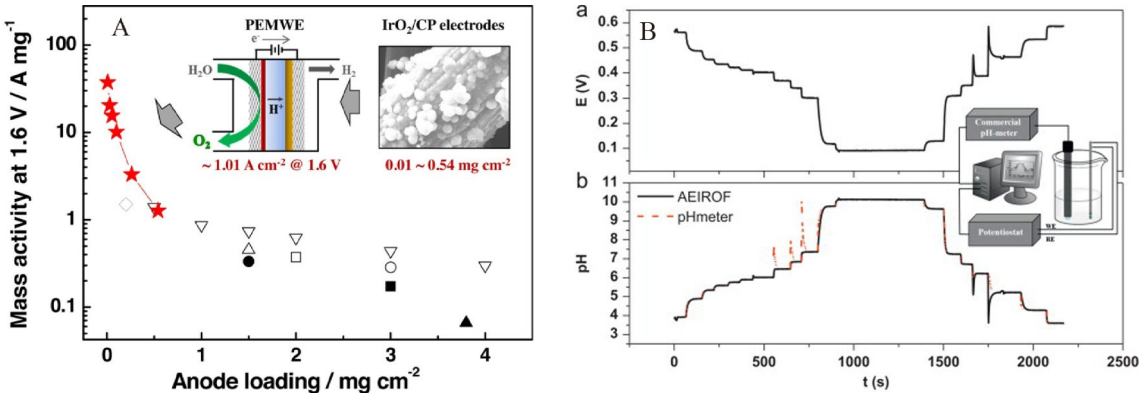

图 1 (A) IrO_2/CP 电极(氧化铱电沉积制备法)在水电解设备中的应用[9]。经许可转载,版权所有 2015 Applied Catalysis B: Environmental。(B) pH 传感微电极在溶液 pH 值测试中的应用[10]。经许可转载,版权所有 2013 Biosensors and Bioelectronics。(网络版彩图)

Figure 1 Applications of iridium oxide electrodes with anodic electrodeposition: (A) as anodes in polymer electrolyte membrane water electrolysis[9]. Reprinted with permission, Copyright 2015 Applied Catalysis B: Environmental. (B) as the pH sensing microelectrode[10]. Reprinted with permission, copyright 2013 Biosensors and Bioelectronics. (color on line)

的沉积量为 0.1 mg·cm^{-2} 时，电解效率测试表现最佳,可实现 IrO_2 的最大利用率。

作者课题组主要在 DSA 阳极的电沉积制备技术方面做了研究。研究表明,电沉积法所制备的氧化铱钛电极，与传统热分解法所制钛基氧化铱电极相比,具有更优秀的电催化活性,且制备过程相对简易,参数可控,具有良好的研究价值及发展潜力。作者课题组还将该电极应用于污泥脱水电解器中[12],实验发现,与传统热分解法制备的氧化铱钛电极相比，使用电沉积法制备的氧化铱电极的污泥脱水电解器的污泥脱水效率更高，提升了 10 个百分点(如图 2 所示)。

2.1 沉积液配方

沉积液中的活性成分主要有氯亚铱酸盐(III)、氯铱酸盐(IV)、硫酸亚铱酸盐(III)和硫酸铱酸盐(IV)等 Ir 化合物[13,14]。表 2 列举了目前主要研究的

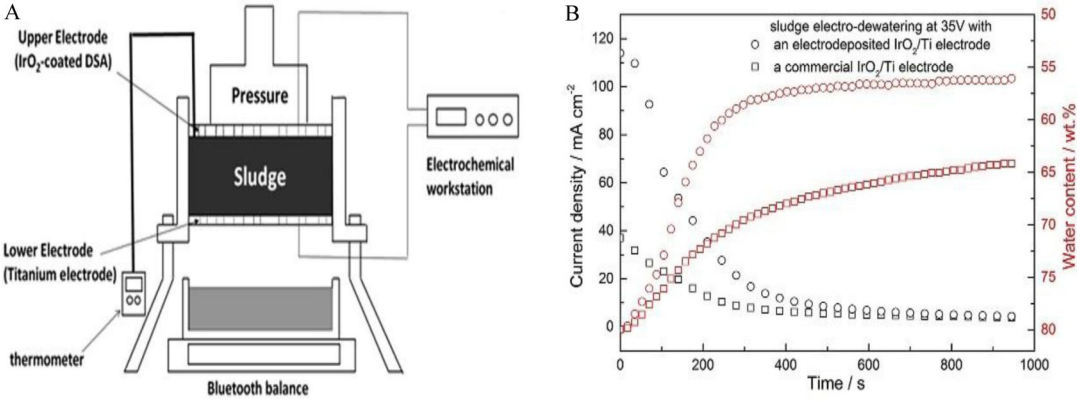

图 2 (A)氧化铱钛电极在污泥脱水电解器中应用;(B)污泥脱水电解器效率[12]。经许可转载,版权所有 2018 Electrochimica Acta。(网络版彩图)

Figure 2 (A) Configuration of laboratory-scale sludge dewatering electrolyser, (B) Performances of sludge dewatering electrolysers with an electrodeposited IrO_2/Ti electrode and a commercial product with voltage 35 V[12]. Reprinted with permission, Copyright 2018 Electrochimica Acta. (color on line)

几种沉积液配方。如表 2 所示,目前所有的沉积液配方都是基于上述铱盐展开研究的，主要是利用三价铱盐或四价铱盐配合基的氧化还原。根据其电沉积转换原理,分为两种过程:一种是利用三价铱盐转变为稳定的四价铱盐，通过四价铱盐配合基阴离子集团的还原性能吸收电子，发生氧化反应,转变为气体等其它物质,铱以二氧化铱的形式沉积在基底上[15-17]。另一种则直接用三价铱盐进行电沉积,使铱发生氧化反应,直接沉积在基底上,该方法在电沉积过程容易受到空气影响，自行氧化,导致沉积液变质,不稳定[18,19]。除铱盐活性成分外,沉积液中的络合剂也很重要,有利于提高活化极化,获得致密均匀沉积层,防止可溶性阳极钝化等。根据基底材料性质的不同,如何选择适宜的络合剂,调节沉积液的配方及配比是关键所在。

作者课题组以 Yamanaka[17]、Toniolo[20]等的沉积液配方为基础,对沉积液做了改进,以更好的适应钛基底的氧化铱电沉积,详见表 3。草酸的添加是为了与 Ir(III)形成草酸铱络合物,K_2CO_3 主要起调节 pH 作用以及形成稳定的 Ir(III)复杂配合物。

表 2 氧化铱电沉积沉积液配方

Table 2 Electrodeposition recipes of iridium oxide electrodes

Author	Composition of deposition solution	Instruction	Deposition Mechanism
Baur[18]	$IrCl_4$、C_2H_5OH、HCl、NaOH	C_2H_5OH: reduction;NaOH:regulate pH	$IrCl_4^{2-} + C_2H_5OH \rightarrow Ir(OH_2)_2Cl^-$ $Ir(OH_2)_2Cl^- \rightarrow Ir_2O_3 \cdot xH_2O$
Toniolo[20]	$IrCl_4 \cdot xH_2O$、H_2O_2(30wt.%) Oxalic acid、K_2CO_3	$H_2C_2O_4$: As complex; K_2CO_3: regulate pH; H_2O_2: improve deposition efficiency	$[Ir(C_2O_4)(OH)_4]^{2-} \rightarrow$ $IrO_2 + 2CO_2 + 2H_2O + 2e^-$
Michel[21]	$IrCl_3$、Oxalic acid、K_2CO_3	$H_2C_2O_4$: As complex; K_2CO_3: regulate pH;	$[Ir(C_2O_4)(OH)_4]^{3-} \rightarrow$ $[Ir(C_2O_4)(OH)_4]^{2-} + e^-$ $[Ir(C_2O_4)(OH)_4]^{2-} \rightarrow IrO_2 + 2H_2O + 2CO_2 + e^-$
Zhang Xing[22]	$(NH_4)_2IrCl_6$ (10g/L) Boric acid (40g/L) Sodium malonate	Boric acid: As solvent; Sodium malonate: Improving Stabilization	-

涉及的化学反应如下：

$[IrCl_6]^{3-} + 3C_2O_4^{2-} \rightarrow [Ir(C_2O_4)_3]^{3-} + Cl^-$

$[Ir(C_2O_4)_3]^{3-} + 4OH^- \rightarrow [Ir(C_2O_4)(OH)_4]^{3-} + 2C_2O_4^{2-}$

$[Ir(C_2O_4)(OH)_4]^{3-} \rightarrow [Ir(C_2O_4)(OH)_4]^{2-} + e$

$[Ir(C_2O_4)(OH)_4]^{2-} \rightarrow IrO_2 + 2H_2O + 2CO_2 + e$

沉积过程分为两步电沉积，首先三价铱的复杂配合物在电场作用下失去电子，转变为四价铱复杂配合物，吸附在电极表面，然后进一步失去电子，以氧化铱的形式沉积在基底上，草酸络离子则转变为二氧化碳。在以较大面积钛(100 mm × 100 mm, TA2)为基底电沉积氧化铱时发现，阳极发生副反应，大量析氧，导致氧化铱沉积不稳定，沉积层粗糙、不平整。除此之外，沉积液还存在稳定性问题，这与 Yan-Hua 等[23]研究相吻合，即氧化铱沉积液放置一定时间后，会产生沉淀，沉积液失效。在王锦鹏等[24]研究中发现，氧化铱沉积液对有机杂质非常敏感，会导致沉积液中局部低电流密度区，使所沉积金属不能均匀地沉积在工件表面上，影响沉积层质量。

2.2 基底材料的选择及处理

关于氧化铱电沉积基底，一般多为碳布、ITO(导电玻璃)等材料，金属基底多为铂、不锈钢、钛等。如图 3 所示，通过 SEM(scanning electron microscope)表征了不同基底上电沉积的氧化铱沉积层形貌，均为循环伏安法下沉积制备。(图 3D 较为特殊，采用了模板化电化学沉积工艺，即预先在基底上化学沉积一层多孔 ZnO，再采用循环伏安法电沉积氧化铱，制备纳米 IrO_x 薄层)氧化铱电极作为固体电极的一种，其沉积层形貌受固体电极表面活性影响，固体金属电极表面活性与表面的固体状态性质(结晶学性质和电子性质)密切相关。因此，既使同一沉积条件下，基底材料不同，沉积层结晶取向不同，形貌各异。

钛及其合金具有密度小、强度高、耐腐蚀、耐高温等优异性能，是 DSA 的基底材料，可广泛适应于各种严苛环境。钛作为单向阀型金属，整体呈“钝性”，不易于金属电沉积，通常需要预处理。其电沉积工序比较复杂：喷沙→除油→侵蚀→活化→浸镀或电解预镀→电沉积→热处理[27]。如何利用钛基的活化，是金属电沉积的关键步骤。为解决此问题，Zhenwei Yan[28]、Aravind[29]、Huang[30]等研究了利用草酸蚀刻的方法去除钛基表面上氧化膜，便于后续电沉积工艺的进行。Nishanthi[31]、Alves[32]等则研究了钛的阳极氧化，使表面生成 TiO_2 纳米管阵列，通过调节电压，极化液浓度等调节控制 TiO_2 纳米管尺寸，此预处理手段可为后续氧化铱的沉积提供更好的依附点，提升氧化铱沉积层与基底的结合力，增大基底活性表面积等。这为钛基底氧化铱电沉积提供了一种很好的预处理思路。

基于上述研究调查，作者课题组通过阳极氧化预处理钛基底后再电沉积氧化铱，结果发现[33]，与草酸蚀刻预处理相比，经阳极氧化预处理后电沉积制备的钛基氧化铱电极的沉积层形貌更加均一化，氧化铱晶粒更细致，如图 4A 所示。电极的电耐久性也显著提高(如图 4D 所示，经 0.5wt.%氢氟酸阳极氧化预处理的电沉积氧化铱钛电极加速老化寿命可达 139 h，而经草酸蚀刻预处理的为 19 h)。

2.3 电沉积方式

关于氧化铱的电沉积方式，据文献调查，主要有恒电流法、恒电压法、循环伏安法等三种模式。恒压恒流体系，即让某种控制形式的电流/电压稳定持续经过电极，并测定相应的电极电位/电流，沉积层质量与电压/电流的大小相关。循环伏安法则让电极电位按某种控制的形式偏离平衡电位，同时测量电极系统的电流、电量，使电解质中铱盐有序沉积在基底上，该法下沉积的氧化铱层质地均

表 3 作者课题组氧化铱电沉积条件

Table 3 Electrodeposition conditions of iridium oxide electrode for the author.

Deposition recipes	Deposition condition
The molo ratio of oxalate and $IrCl_3$ is 5:1	Potentiostatic techniques: 0.8 V
Adjust pH to 10.2 with K_2CO_3	Temperature: Ambient
Iridium ion concentration: 4 mmol·L^{-1}	Stirring: Magnetic
The solution was kept at 40 ℃ for 4 d to allow stabilization.	Atmosphere: Air
	Deposition time: 30 min

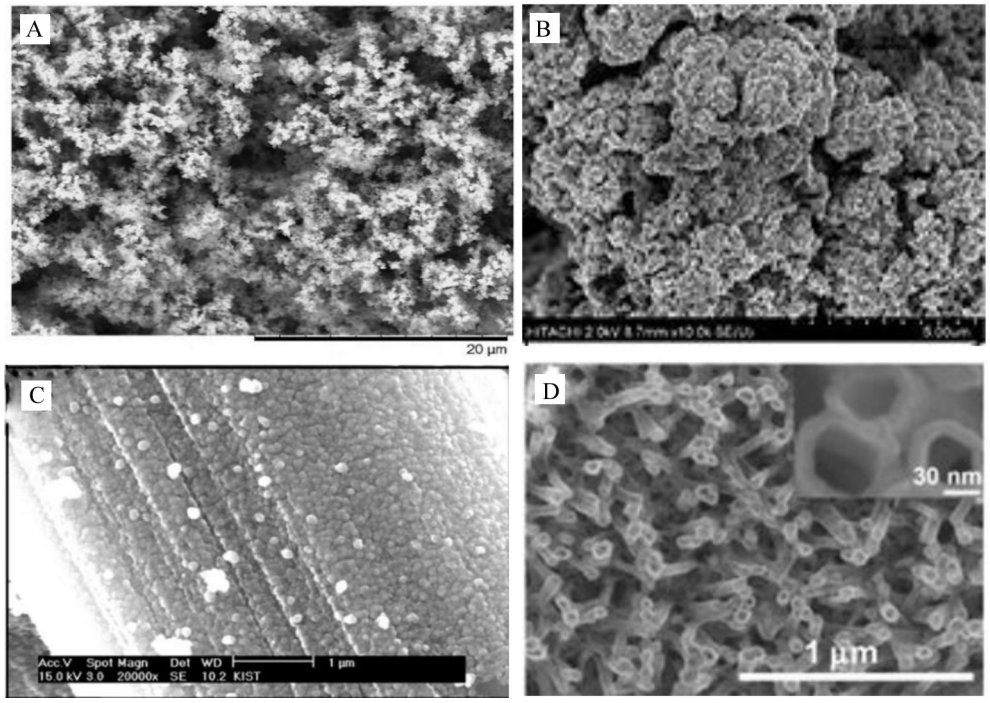

图 3 SEM 表征不同基底上氧化铱沉积层形貌:(A) Ti 基底[12]。经许可转载,版权所有 2018 Electrochimica Acta。(B) 不锈钢基底[25]。经许可转载,版权所有 2013 International Journal of Electrochemical Science。(C) CP 基底[9]。经许可转载,版权所有 2015 Applied Catalysis B: Environmental。(D) ITO 基底[26]。经许可转载,版权所有 2013 Journal of Electroanalytical Chemistry。

Figure 3 SEM images of iridium oxide electrodeposition on different substrates for (A) Titanium[12]. Reprinted with permission, Copyright 2018 Electrochimica Acta. (B) Stainless steel[25]. Reprinted with permission, Copyright 2013 International Journal of Electrochemical Science. (C) Carbon paper[9]. Reprinted with permission, Copyright 2015 Applied Catalysis B: Environmental. (D) ITO substrate[26]. Reprinted with permission, Copyright 2013 Journal of Electroanalytical Chemistry.

匀,具有特殊结构,可进行纳米微沉积,但相应实验条件较为苛刻,操作难度大。罗远辉等[34]采用恒电流法在不锈钢片上电沉积氧化铱,研究表明,随着电流密度的增大, 镀铱层质量先变好后变差。Steegstra[35]则研究发现电沉积的电流密度不宜过高,高电流密度虽然有利于沉积速度的提高,但会降低电流效率, 不易沉积厚层, 所以电流密度在 0.15 A·dm^{-2} 左右为最佳。Meyer 等[36]研究了不同扫速下氧化铱电沉积动力学行为, 即一定电压范围内,电流随时间变化情况,以此来参考恒电位位法的电动势。随着扫速增大,其峰电流也随之增大,最终确定为 0.8 V 下 20 mV·s^{-1} 恒电压电沉积。Yamanaka[37]通过循环伏安法研究了阳极电沉积氧化铱的电化学行为,Jin Hu[11]参考其法在 Pt 上沉积了氧化铱薄膜(-0.7 V ~ 0.7 V),如图 5 所示,沉积过程中出现两个氧化峰:A1 和 A2, 对应着沉积过程 Ir(III)/Ir(IV)和 Ir(IV)/Ir(V)的氧化反应。电沉积方式不同,沉积层质量存在差异,选择合适的沉积方式有利于电解质中活性成分铱的传质效率提高,从而提升沉积层质量。一般而言,对于大的工件,宜采用恒电压/电流法,沉积效率相对较高,易操作。而对于精细微小工件,则采用循环伏安法较佳。

2.4 电沉积时间

尽管氧化铱电沉积存在沉积层薄且质量不高的缺陷,但在沉积层达到极限厚度前,随着电沉积时间增加,沉积层质量趋于优化,这是电沉积本身性质所决定的。随着沉积层厚度增加,电极表观形貌随之变化,对溶液中离子的感应接触也更加灵敏,其中溶液中的铱盐离子会优先沉积到薄弱层去,从而使整个沉积层更加均一化、优质化。Yousefpour 等[38]研究了钛上电沉积混合金属层(RuO_2-IrO_2-TiO_2),通过不同层数沉积发现,随着沉积层增加,沉积层质量得到明显改善,晶粒细化,均质性提高。Wang 等[39]研究发现,随着电沉积时间增加,氧化铱电极的交换电流密度减小。这是由于随着电沉积时间延长,镀液消耗,铱盐离子浓度减

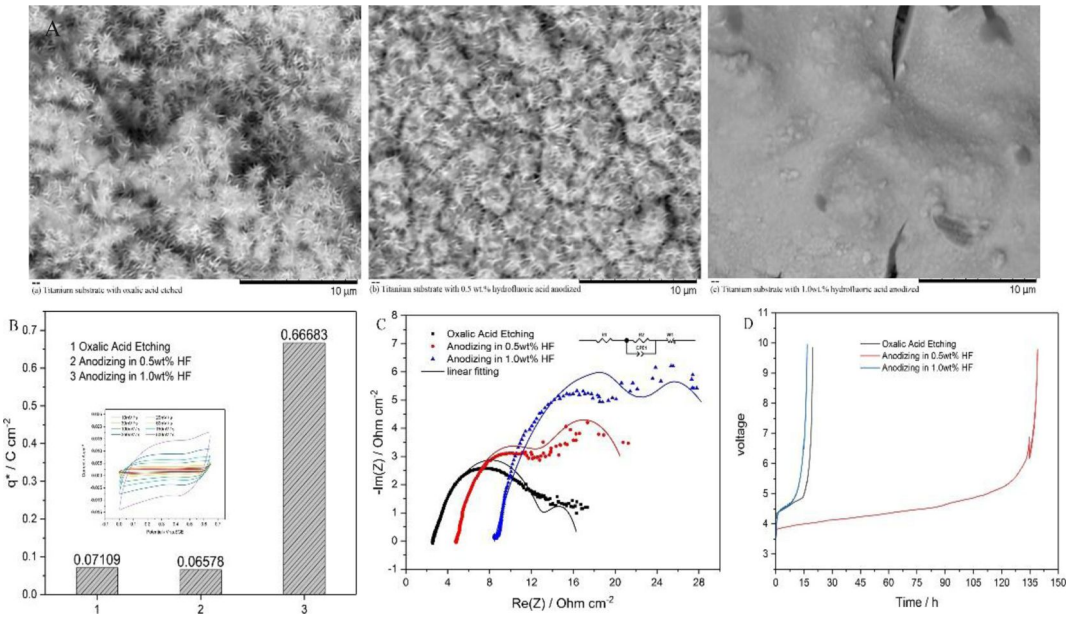

图 4 经草酸蚀刻、0.5wt.%、1.0wt.%氢氟酸阳极氧化预处理的钛基氧化铱电极的 (A) 沉积层形貌 SEM 表征,(B) 循环伏安法及其伏安电荷容量 q*,(C) 阻抗谱测试结果,(D) 加速老化寿命[33]。经许可转载,版权所有 2020 Electrochimica Acta.(网络版彩图)

Figure 4 (A) SEM images, (B) cyclic voltammograms and voltammetric charge diagrams, (C) Nyquist diagrams and (D) accelerated life performance curves of electrodeposited IrO_2/Ti electrodes with oxalic acid deposited, 0.5wt.% and 1.0wt.% hydrofluoric acid anodized[33]. Reprinted with permission, Copyright 2020 Electrochimica Acta. (color on line)

小,电沉积效率下降。在电沉积过程中,应适当考虑电解质补充,沉积液稳态浓度维持问题。Jin Hu[11]采用循环伏安法电沉积制备氧化铱薄膜, 随着循环圈数增加,氧化铱薄膜形貌清晰,表明可通过增加循环圈数,即增加沉积时间,实现氧化铱薄膜沉积层的可控生长。Meyer[36]、Lattach[40]、Salimi[41]等也通过该法研究了氧化铱的电沉积,并提出 CSCC(cathodic charge storage capacity)值,即一定扫速下,阳极界面电荷数量。研究发现,随着循环圈数增加 CSCC 值变大,有利于沉积层紧密度的提升。

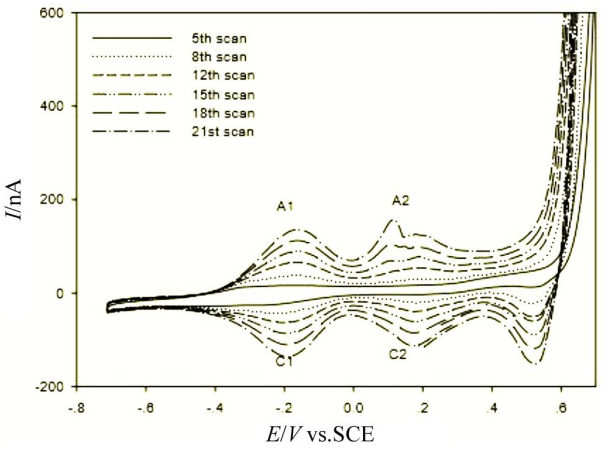

图 5 铂微电极上氧化铱生长的循环伏安曲线图[11]。经许可转载,版权所有 2008 University of Southampton。

Figure 5 Cyclic voltammograms for the growth of iridium oxide on Pt microelectrode[11]. Reprinted with permission, Copyright 2008 University of Southampton.

3 面临的挑战

目前, 钛基氧化铱电极电沉积制备技术的研究还处于初级阶段, 尤其是在 DSA 阳极制备方法上的应用方面,相对匮乏。距工业化应用还面临着很多问题。

第一,沉积层质量问题。根据调研,目前以钛为基底的氧化铱电沉积技术, 其沉积层普遍存在不致密,薄且脆,电解耐久性差,不成膜等问题。而且大多数研究只关注了沉积层的的催化活性问题,相较于传统铱钽涂层,其表现优异,但沉积层寿命往往很短。以 Yousefpour[38]的研究为例,其最好的氧化铱沉积层寿命也只有 15000 s,即 4.16 h,更多研究则未涉及沉积层的寿命问题。因此,如何提高钛基氧化铱沉积层的质量, 重点是延长其使用寿命, 达到与传统热分解法所制氧化铱涂层钛

电极相同水平，这也是电沉积法制备氧化铱钛电极的关键核心所在。通过改变沉积方式,比如脉冲电沉积法[42]、电位阶跃法,提升镀层致密度,增大其耐久性；或者多种工艺组合，比如热分解法与电镀,在沉积层表面刷涂一层惰性层,减缓其侵蚀速度,从而延长使用寿命。也可通过共沉积其他惰性组分,比如 Ta[43]、稀土元素等,提升沉积层质量。

第二,沉积层与基底结合能力。由于钛基材的特殊性质，致使氧化铱沉积层与基底结合力相对微弱,基底易钝化,进一步加剧电极失效速度。解决氧化铱沉积层与钛基底的结合力问题，是提高电沉积法制备氧化铱钛电极质量的另一关键所在。已知的手段主要是通过对钛基材进行预处理来进行改善,除阳极氧化外,还有溶胶-凝胶法、氢热处理等。也可考虑通过添加一个中间层,即在钛基表面覆盖一层其它贵金属氧化层后再电沉积氧化铱,或者添加某种添加剂,增大沉积层与基底的粘合性。再者,预先沉积其他金属,比如 RuO_2[44],通过增加氧化铱与钛基材的强结合点位来提升其整体沉积层与基地的结合能力。关于氧化铱和二氧化钛，有相关新进研究制备了 IrO_2 包覆 TiO_2 核壳微粒[45],阐述了二者构效机制,表明氧化铱和钛的某种特殊结合在水溶液电解催化氧化存在优势,或可为钛上氧化铱的电沉积突破提供指导。

第三,电沉积过程动力学研究。有关于氧化铱钛上电沉积过程沉积层的形貌变化规律、影响因素以及作用机理尚未有相应成果生成，研究也相对较少,无法为实际电沉积提供理论指导,从而进一步优化钛基氧化铱电极电沉积制备方法。其次,电沉积法对于整体电极质量的影响作用机理也不甚明晰,需要更深入研究。可通过利用原位电化学手段进行分析,并结合 COMSOL 等软件模拟其过程,逐步完善整个电沉积过程的动力学研究,建立相应理论知识体系，进一步为实现其工业化应用提供指导。

第四,工业应用。目前钛基氧化铱电沉积主要停留于实验初级研究阶段。虽然其作为氧化铱全固态金属 pH 值敏感电极应用相对较成熟,属于精细化微小工艺。但在大型电极电沉积制备方面的研发几乎为零,距成熟的市场应用相差甚远。若要实现钛基氧化铱电沉积的工业应用，即电镀法制备大型工业电极,还需考虑镀液维稳,电镀槽结构设计,工艺流程规划等一系列问题。

4 结　语

本文系统地论述了氧化铱电沉积制备技术的研究进展,重点讨论了其作为钛基氧化铱电极的电沉积制备技术研究概况及其面临的主要问题,并结合作者课题组所作的相关工作提出一些建议。

钛基氧化铱电极电沉积制备技术作为一种新兴技术,具有环保可持续发展等工艺特点,不论是从工业发展还是科学技术进步角度，都十分具有现实意义及研究价值,应用前景广阔。首先,据市场调查，目前在售的铱钽涂层钛阳极 99%为传统热分解法所制,该法依赖人力刷涂,人工成本高,工艺相对较落后。且为保证电极质量,涂层中贵金属铱含量较高,增加了电极成本。不论是市场开发还是工业制造技术升级，都迫切需要氧化铱钛电极制备技术的革新。其次,随着科学技术的进步,未来电极制造工艺的高自动化、机械化是其发展的必然趋势,而目前主流工艺无法顺应这一趋势,势必会被淘汰。再次,电沉积法可实现通过增加镀液回收工艺使整个电极制造流程可实现循环,从而节约氧化铱钛电极制备的贵金属的投入，降低成本。与涂层相比,镀层可实现整个电极基底均匀地覆盖、成膜,有利于减缓实际电极使用时的恶劣环境对钛基材的腐蚀，便于后续电极回收利用,实现钛基氧化铱电极制造工艺的绿色化、无害化、资源循环化发展,符合国家对工业发展的要求。

参考文献(References):

[1] Scialdone O, Randazzo S, Galia A, Filardo G. Electrochemical oxidation of organics at metal oxide electrodes: The incineration of oxalic acid at IrO_2-Ta_2O_5 (DSA-O_2) anode[J]. Electrochim. Acta, 2009, 54(4): 1210-1217.

[2] Huang C A, Yang S W, Chen C Z, Hsu F Y. Electrochemical behavior of IrO_2-Ta_2O_5/Ti anodes prepared with different surface pretreatments of Ti substrate[J]. Surf. Coat. Technol., 2017, 320: 270-278.

[3] Krysa J, Kule L, Mráz R, Rousar I. Effect of coating thickness and surface treatment of titanium on the properties of IrO_2-Ta_2O_5 anodes[J]. J. Appl. Electrochem., 1996, 26(10): 999-1005.

[4] Xiao J, Wu X, Yu W B, Liang S, Yu J W, Gu Y Y, Deng H L, Hu J K, Xiao K K, Yang J K. Migration and distribution of sodium ions and organic matters during electro-dewatering of waste activated sludge at different dosages of sodium sulfate[J]. Chemosphere, 2017: 189: 67-75.

[5] Yu J G, Zhao X J, Zhao Q N. Photocatalytic activity of

nanometer TiO_2 thin films prepared by the sol-gel method [J]. Mater. Chem. Phys., 2001, 69(1-3): 25-29.

[6] Terabe K, Kato K, Miyazaki H, Yamaguchi S, Imai A, Iguchi Y. Microstructure and crystallization behaviour of TiO_2 precursor prepared by the sol-gel method using metal alkoxide[J]. J. Mater. Sci., 1994, 29(6): 1617-1622.

[7] Thanawala S S, Baird R J, Georgiev D G, Auner G W. Amorphous and crystalline IrO_2 thin films as potential stimulation electrode coatings[J]. Appl. Surf. Sci., 2008, 254(16): 5164-5169.

[8] Labou D, Slavcheva E, Schnakenberg U, Neophytides S. Performance of laboratory polymer electrolyte membrane hydrogen generator with sputtered iridium oxide anode[J]. J. Power Sources, 2008, 185(2): 1073-1078.

[9] Lee B S, Ahn S H, Park H Y, Choi I, Yoo S J, Kim H J, Henkensmeier D, Kim J Y, Park S, Nam S W, Lee K Y, Jang J H. Development of electrodeposited IrO_2 electrodes as anodes in polymer electrolyte membrane water electrolysis[J]. Appl. Catal. B - Environ., 2015, 179: 285-291.

[10] Pratsalfonso E, Abad L, Casanpastor N, Gonzalo-Ruiz J, Baldrich E. Iridium oxide pH sensor for biomedical applications. Case urea-urease in real urine samples[J]. Biosens. Bioelectron., 2013, 39(1): 163-169.

[11] Jin H. Fabrication, characterisation, and optical applications of electrochemically deposited nanostructured IrO_x films[D]. Southampton: University of Southampton, 2008.

[12] Zhang Y L, Cao M M, Lü H, Wei J C, Gu Y Y, Liu D G, Zhang W B, Ryan M P, Wu X. Electrodeposited nanometer-size IrO_2/Ti electrodes with 0.3 mg IrO_2 cm^{-2} for sludge dewatering electrolysers[J]. Electrochim. Acta, 2018, 265: 507-513.

[13] Wang J, Rivas G, Chicharro M. Glucose microsensors based on electrochemical deposition of iridium and glucose oxidase onto carbon fiber[J]. J. Electroanal. Chem., 1997, 439: 55-61.

[14] N Ther J, K Ster F, Freudenberger R, Schoberl C, Lampke T. Electrochemical deposition of iridium and iridium-nickel-alloys[M]. IOP Conference Series: Materials Science and Engineering, 2017, 181: 012041.

[15] Jian X H, Tsai D S, Chung W H, Huang Y S, Liu F J. Pt-Ru and Pt-Mo electrodeposited onto Ir-IrO_2 nanorods and their catalytic activities in methanol and ethanoloxidation[J]. J. Mater. Chem., 2009, 19(11): 1601-1607.

[16] Yagi M, Tomita E, Kuwabara T. Remarkably high activity of electrodeposited IrO_2 film for electrocatalytic water oxidation[J]. J. Electroanal. Chem., 2005, 579(1): 83-88.

[17] Yamanaka K. Anodically electrodeposited iridium oxide films (AEIROF) from alkaline solutions for electrochromic display devices[J]. Jpn. J. Appl. Phys., 1989, 28(4): 632-637.

[18] Baur J E, Spaine T W. Electrochemical deposition of iridium (IV) oxide from alkaline solutions of iridium(III) oxide[J]. J. Electroanal. Chem., 1998, 443(2): 208-216.

[19] Bezbaruah A N, Zhang T C. Fabrication of Anodically Electrodeposited Iridium Oxide Film pH Microelectrodes for Microenvironmental Studies[J]. Anal. Chem., 2002, 74(22): 5726-5733.

[20] Casella I G, Contursi M, Toniolo R. Anodic electrodeposition of iridium oxide particles on glassy carbon surfaces and their electrochemical/SEM/XPS characterization[J]. J. Electroanal. Chem., 2015, 736: 147-152.

[21] Petit M A, Plichon V. Anodic electrodeposition of iridium oxide films[J]. J. Electroanal. Chem., 1998, 444(2): 247-252.

[22] Zhang X(张新), Luo Y H(罗远辉), Li X Y(李兴彦). Effect of some factors in iridium plating on electroplated coating surface[J]. Met. Funct. Mater.(金属功能材料), 2012(4): 46-49.

[23] Shi Y H, Meng H M. Electrochemical behavior of IrO_2 electrodes in the anodic electrodeposition of MnO_2[J]. Acta Phys.-Chim. Sin., 2011, 27(2): 461-467.

[24] Wang J P(王锦鹏), Zhong X M(钟学明), Teng L J(滕乐金), Zhao Y(赵洋). Discussion on removal of the micropotassium from the solution of dihydrogen hexachloroiridate(IV)[J]. G D Chem.(广东化工), 2008, 35(7): 23-26.

[25] Kakooei S, Ismail M C, Wahjoedi B A. Electrochemical study of iridium oxide coating on stainless steel substrate [J]. Int. J. Electrochem. Sci., 2013, 8(3): 3290-3301.

[26] Zhao C X, Yu H T, Li Y C, Li X H, Ding L, Fan L Z. Electrochemical controlled synthesis and characterization of well-aligned IrO_2 nanotube arrays with enhanced electrocatalytic activity toward oxygen evolution reaction[J]. J. Electroanal. Chem., 2013, 688: 269-274.

[27] Sun Z H(孙志华), Liu Y H(刘佑厚), Zhang X Y(张晓云), Tang Z H(汤智慧), Liu M H(刘明辉). A review of electroplating technology on titanium and titanium alloys [J]. Corros. Sci. Prot. Technol.(腐蚀与防护), 2005, 26 (11): 493-496.

[28] Yan Z W, Zhao Y W, Zhang Z Z, Li G, Li H C, Wang J S, Feng Z Q, Tang M Q, Yuan X J, Zhang R Z, Du Y Y. A study on the performance of IrO_2-Ta_2O_5 coated anodes with surface treated Ti substrates[J]. Electrochim. Acta, 2015, 157: 345-350.

[29] Aravind P, Selvaraj H, Ferro S, Sundaram M. An integrated (electro and bio-oxidation) approach for remediation of industrial wastewater containing azo-dyes: Under-

standing the degradation mechanism and toxicity assessment[J]. J. Hazard. Mater., 2016, 318(15): 203-215.

[30] Huang C A, Yang S W, Lai P L. Effect of precursor baking on the electrochemical properties of IrO_2-Ta_2O_5/Ti anodes[J]. Surf. Coat. Technol., 2018, 350: 896-903.

[31] Nishanthi S T, Iyyapushpam S, Padiyan D P. Role of water content in anodization of titanium to fabricate TiO_2 nanotubes and its properties[C]//IEEE, International Conference on Advanced Nanomaterials and Emerging Engineering Technologies (ICANMEET), Chennai, INDIA, Jul 24-27, 2013: 320-323.

[32] Alves S A, Patel S B, Sukotjo C, Mathew M T, Filho P N, Celis J P, Rocha L A, Shokuhfar T. Synthesis of calcium-phosphorous doped TiO_2 nanotubes by anodization and reverse polarization: A promising strategy for an efficient biofunctional implant surface[J]. Appl. Surf. Sci., 2017, 399: 682-701.

[33] Wu D D, Wu X, Zhang Y L. A study on Ti anodic pretreatment for improving the stability of electrodeposited IrO_2 electrode[J]. Electrochim. Acta, 2020, 338: 135793.

[34] Zhang X(张新), Luo Y H(罗远辉), Li X Y(李兴彦). Research progress of iridium electroplating technology[J]. Met. Funct. Mater.(金属功能材料), 2012, 2: 58-61.

[35] Steegstra P, Ahlberg E. Involvement of nanoparticles in the electrodeposition of hydrous iridium oxide films[J]. Electrochim. Acta, 2012, 68: 206-213.

[36] Meyer R D, Nguyen T H, Twardoch U M, Rauh R D. Electrodeposition of iridium oxide charge injection electrodes[C]//Proceedings of the First Joint BMES/EMBS Conference, October 13-16, 1999, Atlanta, GA, USA. IEEE, c1999: 0-1

[37] Yamanaka K. The electrochemical behavior of anodically electrodeposited iridium oxide films and the reliability of transmittance variable cells[J]. Jpn. J. Appl. Phys., 1991, 30(6): 1285-1289.

[38] Yousefpour M, Shokuhy A. Electrodeposition of TiO_2-RuO_2-IrO_2 coating on titanium substrate[J]. Superlattices Microstruct., 2012, 51(6): 842-853.

[39] Wang W D(王维大), Feng Y L(冯雅丽), Li H R(李浩然), Cai Z L(蔡震雷). Electrodeposition of manganese dioxide on Ti-IrO_2 anode in acidic nitrate medium[J]. J. Northeast. Univ.(东北大学学报), 2014, 35(2): 249-252.

[40] Lattach Y, Rivera J F, Bamine T, Deronzier A, Moutet J C. Iridium oxide-polymer nanocomposite electrode materials for water oxidation[J]. ACS Appl. Mater. Interfaces, 2014, 6(15): 12852-12859.

[41] Salimi A, Alizadeh V, Compton R G. Disposable amperometric sensor for neurotransmitters based on screen-printed electrodes modified with a thin iridium oxide film[J]. Anal. Sci., 2005, 21(11): 1275-1280.

[42] Guo W J(郭文君), Li Z Q(李紫琼), Ke R H(柯若昊), Niu D F(钮东方), Xu H(徐衡), Zhang X S(张新胜). A study of pluse electrodeposition on suppressing the formation of lithium dendrite[J]. J. Electrochem.(电化学), 2018, 24(3): 246-252.

[43] Herrada R A, Acosta-Santoyo G, Sepúlveda-Guzmán S, Brillas E, Sires I, Bustos E. IrO_2 Ta_2O_5 |Ti electrodes prepared by electrodeposition from different Ir:Ta ratios for the degradation of polycyclic aromatic hydrocarbons[J]. Electrochim. Acta, 2018, 263: 353-361.

[44] Jiang B(蒋孛), Zhang L N(张莉娜), Qin X X(秦先贤), Cai W B(蔡文斌). Electrodeposition of RuO_2 layers on TiO_2 nanotube array toward CO_2 electroreduction[J]. J. Electrochem.(电化学), 2017, 23(2): 238-244.

[45] Van Pham C, Buhler M, Knoppel J, Bierling M, Seeberger D, Escalera-Lopez D, Mayrhofer K J J, Cherevko S, Thiele S. IrO_2 coated TiO_2 core-shell microparticles advance performance of low loading proton exchange membrane water electrolyzers[J]. Appl. Catal. B - Environ., 2020, 269: 118762.

Research Progress in Electrodeposition Technology of Titanium-Based Iridium Oxide Electrode

Dan-Dan Wu, Xu Wu*

(*College of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China*)

Abstract: Titanium-based iridium oxide electrode has been widely used in various fields, such as electrocatalytic oxidation, biomedical applications, hydrometallurgical metal recovery, electro-osmotic dewatering, etc. At present, it is mainly prepared by traditional thermal decomposition method, however, which has high cost, cumbersome process, mainly relying on manual labor and cannot be mass-produced yet. It is, therefore, urgently necessary to explore new preparation technologies by focusing on electrodeposition technology, with technological characteristics such as eco-friendly and sustainable development. This article systematically discusses the research progress in iridium oxide electrodeposition preparation technology from the aspects of deposition solution formulation, base material selection and treatment, electrodeposition method and deposition time, etc. Some works and achievements, made by the author's research group, such as a new electrodeposition recipe of titanium-based iridium oxide electrode and the pretreatment of titanium with anodic oxidation for improving the stability of electrodeposited IrO_2 electrode are also presented. The current challenges faced by the electrodeposition preparation technology of titanium-based iridium oxide electrode, including bad coating quality, weak bonding ability between coating and substrate, lack of the study on the theory about dynamic of electrodeposition and the problem of industrial applications are analyzed. Based upon the aforementioned challenges, some suggestions, for example, utilizing optimization of the electrodeposition, multi-deposition process combination, metal (such as tantalum, lanthanum) co-deposition, are given to solve for the problem of coating quality. The process of electrodeposition by utilizing in-situ electrochemical methods, and combined with COMSOL and other software to simulate the process, and then starting from both electrochemical theory and crystal growth theory, as well as the gradually perfect the theoretical research on electrodeposition of iridium oxide on titanium are summarized. Finally, the application prospects and future development directions are highlighted. It is expected that this brief review would offer critical insights and useful guidelines for developing superior electrodeposition technology of titanium-based iridium oxide electrode.

Key words: IrO_2/Ti electrodes; electrodeposition; industrial applications