Corrosion behavior of Ti/Al laminate composites as electrode of chlor-alkali electrolysis

Lixia Wang¹, Limin Sun², Yang Cao³ and Jing Shen¹

Abstract
High-performance electrodes can solve problems of high voltage and large electricity consumption existing in chlor-alkali industry. A Ti/Al laminate composite (named as Ti/Al-LC) with three-layered structure (Ti/Al₃Ti/Ti) is prepared as a new type of anode electrode for chlor-alkali electrolysis. Scanning electron microscope observation shows that the Ti/Al-LC is composited of a thicker inner layer with thickness about 700 μm and two thinner outer layers with thickness about 300 μm. From the X-ray diffraction pattern, it is known that the outer layers consisted of α-Ti and β-Ti phases, while the inner layer consisted of Al₃Ti intermetallic phase. A saturated sodium chloride (NaCl) solution at 70°C is purposely chosen as the corrosion electrolyte to analyze the corrosion behavior of Ti/Al-LC as anode electrode for chlor-alkali electrolysis. Electrochemical tests, including potentiodynamic polarization and electrochemical impedance spectroscopy measurements, on a three-electrode system indicate that the Ti/Al-LC has a low corrosion rate with corrosion current density of 1.94 μA cm⁻² and stable surface passive film in saturated NaCl solution at 70°C.

Keywords
chlor-alkali electrolysis, anode electrode, Ti/Al laminate composites, corrosion resistance, electrochemical impedance spectroscopy

Introduction
The chlor-alkali industry with products of chlorine (Cl₂), hydrogen (H₂) gases, and caustic soda forms a very important component of basic chemical building blocks that are essential for making thousands of downstream chemical products.¹,² With the rapid development of chlorine alkali industry, it becomes an important research subject on how to reduce energy consumption, raise economic benefits, and improve the technology level. One of the ways to solve problems of high voltage and large electricity consumption existing in common electrolyzers is to select high-performance anode and cathode electrodes. Graphite is a traditional and widely used anode electrode in chlorine alkali industry due to its abundance in resources and low price.³,⁴ However, the overpotential of Cl⁻ ions is high, which increases the bath voltage during the electrolytic process. Besides, anode corrosion consumption of graphite not only reduces its useful life span but also blocks the membrane. Dimensional stable anode (DSA) with high selectivity for anodic reactions, good corrosion resistance, and long useful life span has attracted much attention in chlor-alkali industry.⁵,⁶ However, the high cost of DSA, which is composited of a titanium substrate coated by a platinum-group metal (such as ruthenium) oxide and valve metal (such as titanium) oxide mixed coating, is the main disadvantage. In this work, a relatively low-price Ti/Al laminate composite (Ti/Al-LC) with three-layered structure (Ti/Al₃Ti/Ti) is prepared and used as an anode electrode for chlor-alkali electrolysis. The corrosion behavior of Ti/Al-LC is analyzed, and the results show that it has a low corrosion rate with stable surface passive film in saturated NaCl solution at 70°C.

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laminate composite (named as Ti/Al-LC) with three-layered structure (Ti/Al₃Ti/Ti/Ti) is proposed as a new type of anode electrode for chlor-alkali electrolysis. Chlorine and chloride have serious causticity to the electrode, especially the anode electrode in the chlor-alkali industry. Therefore, the corrosion behavior of Ti/Al-LC was evaluated in the chlor-alkali electrolysis environment.

**Experimental section**

**Preparation of the Ti/Al laminate composites**

In this work, the Ti/Al laminate composites with three-layered structure (Ti/Al₃Ti/Ti/Ti) were fabricated using Ti (TC4) and Al foils through vacuum hot-pressing sintering process in a ZRY-60-30 vacuum furnace. Before sintering, two Ti foil samples (thickness 0.5 mm) and one Al foil (thickness 0.7 mm) were pickled to remove the surface oxides, rinsed with deionized water, dried at room temperature, and overlapping placed (Ti/Al/Ti) in the furnace. During the sintering process, firstly, the sintering chamber was vacuumized to 0.01 Pa, then the samples were heated at 950 K, and then loaded a 2 MPa pressure for 10 min. After that, the pressure of the sample was unloaded to 0.5 MPa and the temperature was elevated to 960 K for 5 min to remove the residual liquid Al. Lastly, the loading pressure was increased to 4 MPa at 960 K for 1 h to get the Ti/Al laminate composites.

The crystalline structure of the Ti/Al laminate composites was verified by X-ray diffraction (XRD; D8 Advance, Germany). To analyze the phase composition of the inner layer, XRD test was applied on the inner layer by removing the outer layer of the Ti/Al laminate composites. The cross-sectional morphology as well as the thickness of the Ti/Al laminate composites was analyzed by a scanning electron microscope (SEM; JSM-6490LV, Japan).

**Electrochemical tests**

In the chlor-alkali electrolysis process, an aqueous saturated sodium chloride (NaCl) solution is fed to the anode side of the electrolyzer. The operation temperature is usually about 60–90°C. Therefore, in this research, a saturated NaCl solution at 70°C was purposely used as the corrosion electrolyte. Before electrochemical test, the samples were welded to a copper wire and the backside edges of the specimen were covered with high temperature silica gel, which guaranteed only the Ti surface exposing to the corrosion electrolyte. A three-electrode system comprising of a saturated calomel electrode (SCE) electrode (as the reference electrode), a platinum sheet (as the auxiliary electrode), and the samples (as the working electrode) was applied for the electrochemical tests. The corrosion behavior of the samples was characterized by potentiodynamic polarization on a CHI660E electrochemical workstation. Before each potentiodynamic test, the samples were first stabilized at open-circuit potential (OCP) for 5 min, then started potential sweep from −0.2 V (vs. OCP) to 2.0 V (vs. SCE) with a scanning rate of 10 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out at OCP in a frequency range from 100,000 Hz to 0.01 Hz with the perturbation amplitude of 5 mV. The EIS data were analyzed by ZSimpWin 3.10 software.

**Results and discussion**

**Characterization of the polylaminate coating**

Figure 1(a) shows the cross-sectional SEM morphology of Ti/Al-LC. As observed in the figure, the Ti/Al-LC is composed of three layers: a thicker inner layer with thickness about 700 μm is covered by two thinner outer layers with thickness about 300 μm. Also, the outer layers display well metallurgical adhesion to the inner layer, which is free of defects such as pinhole, micropore, and microcracks. To verify the crystal structure of the outer and inner layers, XRD tests were carried out on the surface and inner layer (removing the outer by grinding) of Ti/Al-LC, respectively. Figure 1(b) depicts the XRD patterns of the surface and inner layer of Ti/Al-LC.
The surface layer texture of the Ti/Al-LC consisted of α-Ti with (002) (2θ = 38.78°), (101) (2θ = 40.51°), and (102) (2θ = 53.31°) reflections and β-Ti phase with (211) (2θ = 71.42°) and (220) (2θ = 82.75°) reflections, which is consistent with the fact that TC4 is a two-phase (α/β) alloy. The thickness of the outer layer is about 300 nm, X-rays are able to penetrate the outer layer. Therefore, the appearance of reflection peak at 2θ = 80.66° on XRD pattern of surface Ti/Al-LC is the Al3Ti phase. The XRD pattern of the inner layer shows that the main phase is Al3Ti intermetallic alloys. It is also observed that no reflection peaks for Al phase have been observed, which indicates a complete reaction of Al foil with Ti. Through the above analysis, the Ti/Al-LC is consisted of two outer TC4 layers and an inner Al3Ti intermetallic layer.

**Corrosion resistance and stability**

Potentiodynamic polarization tests were used to estimate the general corrosion resistance of Ti/Al-LC in saturated NaCl solution at 70°C, as shown in Figure 2(a). It is observed from the potentiodynamic polarization curves that the Ti/Al-LC shows a typical passivation behavior. The polarization curves can be divided into four regions: in the cathode polarization region (curve ab), the current density decreases with increasing potential, and H2 evolution is the main electrochemical process; in the anode polarization region (curve bc), the current density increases with increasing potential and the dissolving of the tested sample is the main electrochemical process. It is different from other passivation metals like stainless steel that the Ti/Al-LC shows no obvious active–passive transition. The Ti/Al-LC is passivated directly in the anode polarization region indicating the easier self-passivating behavior. During the passivation process, a passive film begins to form on the tested sample surface; in the passive region (curve cd), when the potential exceeds point c, the current density stabilizes, the passive film covers the entire surface of the tested sample and the passivation current density is as low as 1.86 μA cm^-2; in the transpassive region (curve de), the current density increases rapidly with increasing potential once the potential surpasses point d (about at 1.5 V), and the passive film dissolves. The corrosion current density Icorr was also obtained by linear polarization method. Results show that the Icorr of Ti/Al-LC is only 1.94 μA cm^-2 in the saturated NaCl solution at 70°C. Such low-corrosion current density can guarantee a long and stable life of Ti/Al-LC in the chlor-alkali industry.

EIS is a quasi-steady-state measurement, which is able to test the electrochemical behavior of electrode without exerting great impact on the electrochemical system due to the low-amplitude perturbation signal. The Nyquist plot for Ti/Al-LC obtained in saturated NaCl solution at 70°C is shown in Figure 2(b). It is observed that Nyquist plot displays one depressed semicircle within the test frequency range (from 100,000 Hz to 0.01 Hz). Figure 2(c) displays Bode plots of Ti/Al-LC. Two peaks are observed on the phase angle versus frequency plot indicating two time constants. Typically, when titanium or its alloy is exposed to the acid corrosive electrolyte, passive films will be formed due to the passivating element Ti. However, under more aggressive corrosion circumstances, the passive films can be destroyed leading to penetration of the electrolyte into the passive film/Ti interface. The electrolyte can pass through the passive film and contact with the passive film/Ti interface directly, and therefore, two time constants appear on the Bode plots. According to the above analysis, an equivalent circuit (Figure 2(d)) is established to fit the impedance spectra of Ti/Al-LC tested in saturated NaCl solution at 70°C, where Rs, Rf, Cdl, Rc, and Cf are
Table 1. Calculated results of EIS spectra for Ti/Al-LC.

| Sample     | $R_s$ (Ω cm²) | $Q_{dl}$ (Ω⁻¹ cm² s⁻¹) | $R_{dl}$ (Ω cm²) | $n_{dl}$ | $Q_t$ (Ω¹ cm⁻² s⁻¹) | $n_t$ | $R_t$ (Ω cm²) |
|------------|---------------|------------------------|------------------|----------|---------------------|-------|---------------|
| Ti/Al-LC   | 18.15         | $6.44 \times 10^{-7}$  | 2.38 $\times 10^7$ | 0.62     | 4.85 $\times 10^{-7}$ | 0.79  | 2327          |

EIS: electrochemical impedance spectroscopy; Ti/Al-LC: Ti/Al laminate composite; $R_s$: solution resistance (between the electrode reference and working electrode); $R_t$: passive film resistance.

denoted as the solution resistance (between the electrode reference and working electrode), charge transfer resistance, double-layer capacitance, passive film resistance, and passive film capacitance, respectively. Typically, due to the nonideal capacitive response of the double layer and passive film, constant phase elements (CPEs) are used to replace the $C_f$ and $C_{dl}$ to calculate the spectra. The CPE impedance can be presented as

$$Z_{CPE} = Q(j\omega)^{-n}$$ (1)

where $Q$, $\omega$, and $n$ are the admittance magnitude of CPE, the angular frequency, and the CPE power, respectively. The calculated results are listed in Table 1. The charge transfer resistance of Ti/Al-LC is $2.38 \times 10^{-7}$ Ω cm², which indicates less electrochemical reactions and stable passive film in chlor-alkali electrolysis operating condition.

Conclusions

A new type of anode electrode Ti/Al-LC with relatively low price for chlor-alkali electrolysis was prepared in this research. The Ti/Al-LC was consisted of two outer TC4 titanium alloy layers with thickness of 300 μm for each layer and an inner Al₃Ti intermetallic layer with thickness of 700 μm. Furthermore, the outer layers displayed well metallurgical adhesion to the inner layer, which was free of defects such as pinhole, micropore, and microcracks. Chlorine and chloride have serious causticity to the electrode, especially the anode electrode in the chlor-alkali industry. A saturated NaCl solution at 70°C was used as the corrosion electrolyte to analyze the corrosion behavior of Ti/Al-LC as anode electrode for chlor-alkali electrolysis. Corrosion current density derived from the potentiodynamic polarization plots was as low as 1.94 μA cm⁻², while the charge transfer resistance calculated from the EIS data was as high as $2.38 \times 10^{-7}$ Ω cm², which can guarantee a long and stable life of Ti/Al-LC in the chlor-alkali industry.

Declaration of conflicting interests

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References

1. Zhao A, Zhong F, Feng X, et al. A membrane-free and energy-efficient three-step chlor-alkali electrolysis with higher-purity NaOH production. *ACS Appl Mater Interfaces* 2019; 11: 45126–45132.
2. Zhao Y, Zhan J, Liu G, et al. Evaluation of dioxins and dioxin-like compounds from a cement plant using carbide slag from chlor-alkali industry as the major raw material. *J Hazard Mater* 2017; 330: 135–141.
3. Figueiredo RS, Bertazzoli R and Rodrigues CA. Copper/carbon/PTFE oxygen-depolarized cathodes for chlor-alkali membrane cells. *Ind Eng Chem Res* 2013; 52: 5611–5615.
4. Chen R, Trieu V, Schley B, et al. Anodic electrocatalytic coatings for electrolytic chloride production: a review. *Z Phys Chem* 2013; 227: 651–666.
5. Trieu V, Schley B, Natter H, et al. RuO₂-based anodes with tailored surface morphology for improved chlorine electroactivity. *Electrochim Acta* 2012; 78: 188–194.
6. Takasu Y, Sugimoto W, Nishiki Y, et al. Structural analyses of RuO₂–TiO₂/Ti and IrO₂–RuO₂–TiO₂/Ti anodes used in industrial chlor-alkali membrane processes. *J Appl Electrochem* 2010; 40: 1789–1795.
7. Yuan MN, Li L and Wang ZJ. Study of the microstructure modulation and phase formation of Ti-Al₃Ti laminated composites. *Vacuum* 2018; 157: 481–486.
8. Cao Y, Zhu S, Guo C, et al. Numerical investigation of the ballistic performance of metal-intermetallic laminate composites. *Appl Compos Mater* 2014; 22: 437–456.
9. Price RD, Jiang F, Kulin RM, et al. Effects of ductile phase volume fraction on the mechanical properties of Ti-Al₃Ti metal-intermetallic laminate (MIL) composites. *Mater Sci Eng A* 2011; 528: 3134–3146.
10. Fang H, Zhang LS, Xing YL, et al. Nanostructured manganese oxide films for high performance supercapacitors. *Int J Electrochem Sci* 2018; 13: 8736–8744.
11. Niu Q, Gao K, Tang Q, et al. Large-size graphene-like porous carbon nanosheets with controllable N-doped surface derived from sugarcane bagasse pith/chitosan for high performance supercapacitors. *Carbon* 2017; 123: 290–298.
12. Wang L, Gao H, Fang H, et al. Effect of methanol on the electrochemical behaviour and surface conductivity of niobium carbide-modified stainless steel for DMFC bipolar plate. *Int J Hydrogen Energ* 2016; 41: 14864–14871.

13. Safdar A, Wei LY, Snis A, et al. Evaluation of microstructural development in electron beam melted Ti-6Al-4V. *Mater Charact* 2012; 65: 8–15.

14. Wang H, Warnken N and Reed RC. Thermodynamic and kinetic modeling of bcc phase in the Ti–Al–V ternary system. *Mater Sci Eng A* 2010; 528: 622–630.

15. Zeng L and Bieler TR. Effects of working, heat treatment, and aging on microstructural evolution and crystallographic texture of α, α′, α″ and β phases in Ti–6Al–4V wire. *Mater Sci Eng A* 2005; 392: 403–414.

16. da Silva SLR, Kerber LO, Amaral L, et al. X-ray diffraction measurements of plasma-nitrided Ti–6Al–4V. *Surf Coat Technol* 1999; 116–119: 342–346.

17. Gao K, Zhao S, Niu Q, et al. Polyaniline nanorods random assembly on sugarcane bagasse pith-based carbon sheets with promising capacitive performance. *RSC Adv* 2019; 9: 17358–17365.

18. Zhang AQ, Zhou JJ, Das P, et al. Revisiting metal electrodeposition in porous anodic alumina: toward tailored preparation of metal nanotube arrays. *J Electrochem Soc* 2018; 165: D129–D134.

19. Wang L, Li L, Shen J, et al. High conductivity and anti-corrosive tantalum surface modified ferritic stainless steel bipolar plate for direct ethanol fuel cell. *Results Phys* 2019; 14: 102394.

20. Jia X, Zhang Y, Zhang L, et al. Controllable synthesis and bifunctional electrocatalytic performance towards oxygen electrocatalytic reactions of Co3O4 nanoflakes/nitrogen-doped modified CMK-3 nanocomposite. *Inorg Chem Commun* 2019; 108: 101–112.

21. Fang H, Meng F, Yan J, et al. Fe3O4 hard templating to assemble highly wrinkled graphene sheets into hierarchical porous film for compact capacitive energy storage. *RSC Adv* 2019; 9: 20107–20112.

22. Fang H, Chen G, Wang L, et al. Facile fabrication of hierarchical film composed of Co(OH)2@Carbon nanotube core/sheath nanocables and its capacitive performance. *RSC Adv* 2018; 8: 38550–38555.

23. Chang J, Gao Z, Wang X, et al. Activated porous carbon prepared from paulownia flower for high performance supercapacitor electrodes. *Electrochim Acta* 2015; 157: 290–298.

24. Wang L, Li L, Liu H, et al. Polylamine TaN/Ta coating modified ferritic stainless steel bipolar plate for high temperature proton exchange membrane fuel cell. *J Power Sources* 2018; 399: 343–349.