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The Current Progress of the Titanium Preparation by Electrolysis in the Room-Temperature Ionic Liquid Electrolytes

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ABSTRACT

Titanium is a beneficial metallic material due to its excellent properties. However, the large-scale application of titanium is inhibited by the high production cost of the Kroll process. To address this challenge, researchers have proposed many new strategies based on electrochemical technology over the past decades. Those electrochemical methods show potential practical value to replace the Kroll process. Nevertheless, many of them are conducted in high-temperature melts, limiting the rapid development of those methods. Accordingly, room-temperature electrolysis in ionic liquid electrolytes was employed in titanium production. At present, there is no systematic and in-depth summary on room-temperature titanium electrolysis, although many pathways in room-temperature melts have been reported. In this review, we briefly outline the development of the titanium electrolysis methods firstly and summarize the room-temperature titanium electrolysis in ionic liquid electrolytes.

Furthermore, we have discussed the fundamental mechanisms and key challenges occurring in room-temperature titanium electrolysis. Finally, we proposed the opportunities and research direction on room-temperature titanium electrolysis. We hope this review will be a valuable roadmap for room-temperature titanium electrolysis.

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1. Introduction

Titanium and its alloys are magnetic metallic materials that are gaining ever-increasing attention in many fields, because of their excellent physicochemical properties, including low density, high specific strength, high melting point, non-toxic, outstanding corrosion resistance, and good biocompatibility. [1]. However, they are still applied as rare metals at present, although the content of titanium in the Earth's crust is not rare. The root for this anomaly is the high production cost of titanium and its alloys via the traditional Kroll process (Figure **1**) [2]. To reduce the production cost, many strategies, including chemical and electrochemical pathways, were proposed. Electrochemical methods attracted more interest because the reduction ability and rate of electrons are more controllable than that of the carbothermic and metallothermic reduction [3]. On the other hand, due to the excellent conductivity, ion mobility, and reaction rate of molten salt, many electrochemical methods for titanium production were conducted in molten salt systems. Here, we listed some well-known methods that include the FFC process [4], OS process [5], USTB process [6], and SOM process [7, 8]. Although all of them take place in molten salt systems, their reaction mechanisms are different. For example, the fundamental reaction of the FFC process is the electro-reduction of the titanium dioxide cathode. However, the cathodic reduction process of titanium dioxide in the OS process is calcium-thermal reduction. The reaction process of the USTB process is similar to the electrorefining process, which relates to the dissolution of anode and deposition of titanium at the cathode.

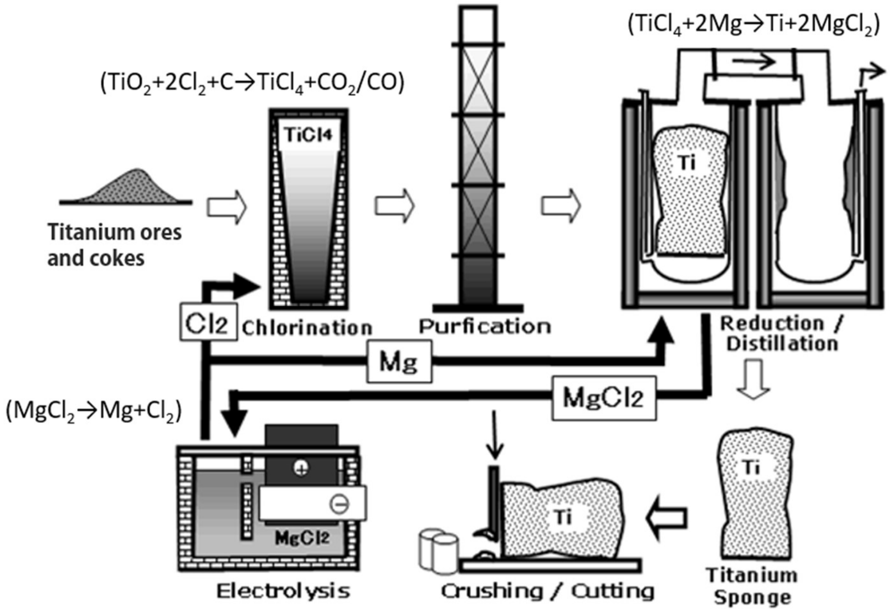

Figure 1: The flowchart of the Kroll process.

Abovementioned methods that are operated in high-temperature molten salts open up the potential ways for reducing the titanium production cost. However, there are some disadvantages of molten salts, such as high corrosivity, high viscosity, and high melting point, which inhibit the large-scale application of those methods. To overcome these demerits, room-temperature ionic liquids (RTIL) were introduced for titanium production.

2. Room-Temperature Titanium Electrolysis in Ionic Liquids

The history of RTIL could date back to the beginning of the 1900s. It has experienced rapid development due to the outstanding physicochemical properties such as low melting point, low pollutant emission, low energy consumption, wide electrochemical window, negligible vapor pressure, high thermal stability, wide electrochemical window [9]. Figure **2** is the photograph of a typical RTIL. At present, RTIL has been widely employed in the chemical industry, energy industry, etc. [10]. The production of titanium and its alloys by electrolysis in RTIL has been proposed for 40 years. In 1981, Hogne Linga *et al*. investigated the electrochemical behavior of Ti^{4+} ions in a basic n-butyl pyridinium chloride-aluminum chloride ionic liquid, and they found that the Ti^{4+} ions can be electro-reduced to Ti^{3+} ions. However, the further reduction process of Ti^{3+} ions was not detected [11]. Meanwhile, metallic titanium could be anodized to yield Ti^{3+} but appears to passivate in the electrolyte. R. T. Carlin *et al*. examined the electrochemistry and chemistry of Ti^{4+} ions in a strongly Lewis acidic $AlCl_3$-1-ethyl-3-methylimidazolium chloride ($AlCl_3$-EtMeImCl) ambient-temperature molten salt in 1990 [12]. Their results showed that Ti^{4+} could be reduced to Ti^{3+} and Ti^{2+}, but Ti^{3+} appeared as the insoluble $TiCl_3$ precipitate adhered on the electrode that could not be furtherly reduced to metallic titanium.

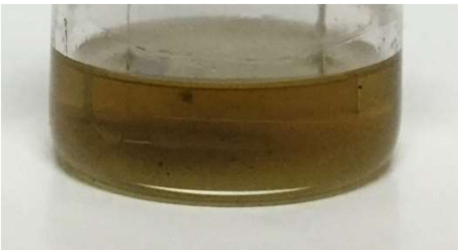

Figure 2: The photograph of a typical RTIL.

In 2003, Tetsuya Tsuda *et al*. also studied the electrochemical chemical behavior of titanium in the $AlCl_3$-EtMeImCl melt at 80 °C [13]. Then, they revealed the cathodic deposition process of Al-Ti alloys at Cu rotating disk and wire electrodes. In saturated solutions of Ti^{2+}, they obtained the Al-Ti alloys containing up to 19% titanium after electrolysis at low current densities. In addition, they found that the titanium content of these alloys decreased with the increase of cathodic current density. In the same year, I. Mukhopadhyay and W. Freyland monitored the electrodeposition of Ti nanowires at the step edge of highly oriented pyrolytic graphite (HOPG) from 0.24 M $TiCl_4$ in the 1-butyl-3-methyl imidazolium bis ((trifluoro methyl sulfonyl) amide at room-temperature by using scanning tunneling microscopy (STM) [14]. They found that Ti^{4+} ions could be reduced to Ti nanowires on the HOPG electrode at a potential of -1.0 V (vs. $[Fc]^+/[Fc]$ redox couple), and they also obtained the Ti nanowires with 10±2 nm width and more than 100 nm length. From 2004 to 2007, researchers from the US Department of Navy applied a series of patents on the titanium extraction from oxidized titanium or titanium dioxide cathodes in a non-aqueous ionic liquid comprising $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride (EMIC) [15, 16]. Because their reduction mechanism is similar to the FFC process, those patents could be seen as the room-temperature FFC process. In 2005, I. Mukhopadhyay, W. Freyland, and their colleagues monitored the electrodeposition process of Ti ions in RTIL by using an in situ STM again [17]. In this case, they studied the cathodic process of Ti^{4+} on an Au (1 1 1) substrate from a nominal 0.24 M $TiCl_4$ in 1-methyl-3-butyl-imidazolium bis (trifluoromethyl sulfone) imide ([BMIm]BTA) melt. They found that $TiCl_4$ could be reduced to $TiCl_2$ and when the cathodic potential was below -1.1 V (vs. $[Fc]^+/[Fc]$), there were 2D $TiCl_3$ precipitates covered on the substrate. However, when the potential was -1.8 V (vs. $[Fc]^+/[Fc]$), a dense layer of metallic titanium with 1-2mm thickness could be obtained on the substrate. At the same time, Yasushi Katayama *et al*. from Keio University investigated the electrochemical reduction of titanium tetrabromide in a hydrophobic 1-*n*-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide (BMPTFSI) at 180 °C [18]. Their results showed that the Ti^{4+} could be reduced to Ti^{3+} and probably Ti^{2+}. In a two-compartment cell, they got some titanium compounds containing $TFSI^-$ anions at -2.3 V. At -3.0 V, they obtained some compounds containing titanium without $TFSI^-$ anions, but it was not identified clearly.

In 2006, some researchers studied the cathodic process of Ti^{4+} ions at an iron substrate in a $BMImBF_4$ ionic liquid with 1 M TiF_4. Their cyclic voltammetry result showed two cathodic peaks corresponding to the reduction process of Ti^{4+} to Ti^{3+} and Ti^{3+} to Ti. However, the XRD result indicated that the cathodic process or cathodic plating was Fe_2Ti alloy, which means that the second cathodic peak may be the underpotential deposition or alloys process of titanium at the iron cathode. In 2007, Yuriy Andriyko and Gerhard E.Nauer [19] examined the cathodic process of titanium tetrachloride in 1-butyl-2,3-dimethyl imidazolium azide ($BMMImN_3$). Cyclic voltammetry and IR spectra results proved that the Ti^{4+} could be reduced to Ti^{3+} only [19]. Similar results were also obtained by Aurbach *et al*. [20], who reported the electrochemical behavior of titanium and Ti^{4+} compounds. Based on the analyses of Raman, UV-vis spectroscopy, ICP, and CHNS elemental, the authors found that metallic titanium could be dissolved and form Ti^{4+}. However, Ti^{4+}ions could be reduced to Ti^{3+}only [20]. At the same time, Jie Ding *et al*. [22] studied the electrochemical deposition of Ti^{4+} in the ethyl-methyl-imidazolium bis(trifluoromethanesulfonyl)amide ionic liquid. Although they found that the pyrrole would introduce the deposition of titanium ions as a nucleation site, they still did not get the bulk metallic titanium [21]. One year later, Jie Ding *et al*. investigated the electrochemical co-deposition of Ti^{x+} ions again [22], in which $TiCl_4$ and $AuCl_3$ were added into ionic liquids together. However, there was still no evidence for the reduction of Ti^{4+} to Ti^0, despite the fact that they obtained thin films with some titanium and gold. In the same year, F. Endres *et al*. checked the ability to electrodeposit titanium at room temperature [23]. For this purpose, they employed three types of RTIL, including 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[EMIm]Tf_2N$), 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)amide ($[BMP]Tf_2N$), and trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)amide ($[P_{14,6,6,6}]Tf_2N$), but unfortunately they concluded that it does not appear possible to reduce Ti^{4+} to metallic titanium. One year later, D. Pradhan and R. G. Reddy investigated the production of Ti-Al alloys by electrolysis in $TiCl_4$-$AlCl_3$-1-1bytyl-3-methyl imidazolium chloride (BMImCl) melt [24]. Although Ti-Al alloys with 15-27 at% Ti content were successfully prepared, $TiCl_3$ passivation on cathode limited the cathodic kinetics and led to very low cathodic current density and bad current efficiency from 25 to 38%.

Entering a new decade, Claire Fournier and Frédéric Favier studied the electrochemical fabrication of nanowires of Zn, Ti, and Si on HOPG in 1-butyl-1-methylpyrrilidinium bistrifluoromethanesulfonimide ($[BMP]NTf_2$) ionic liquid [25]. Their results showed two reduction peaks on the cyclic voltammogram of the 0.1 M $TiCl_4$, corresponding to the reduction of Ti^{4+} to Ti^{2+} and the reduction of Ti^{2+} to Ti^0, respectively. However, they did not give the chemical evidence to prove the metallic titanium further. Soon afterward, Abhishek Lahiri and Rupak Das successfully obtained titanium aluminum alloys in EMIC ionic liquid [26]. In 2016, Chao Qi *et al*. studied the electrodeposition of titanium from an ionic liquid and claimed that titanium ions could be reduced to metallic titanium in some ionic liquid [27]. However, they did not give solid evidence to support their opinion. From 2010 to 2012, Zhang *et al*. [28] and Xu *et al*. [29,30] studied the electrochemical behavior of titanium ions in ionic liquids and prepared some titanium alloys, such as Ti-Zn and Ti-Al alloys (Figure **3**). Although they also wanted to prepare pure titanium from ionic liquids, they did not achieve this aim.

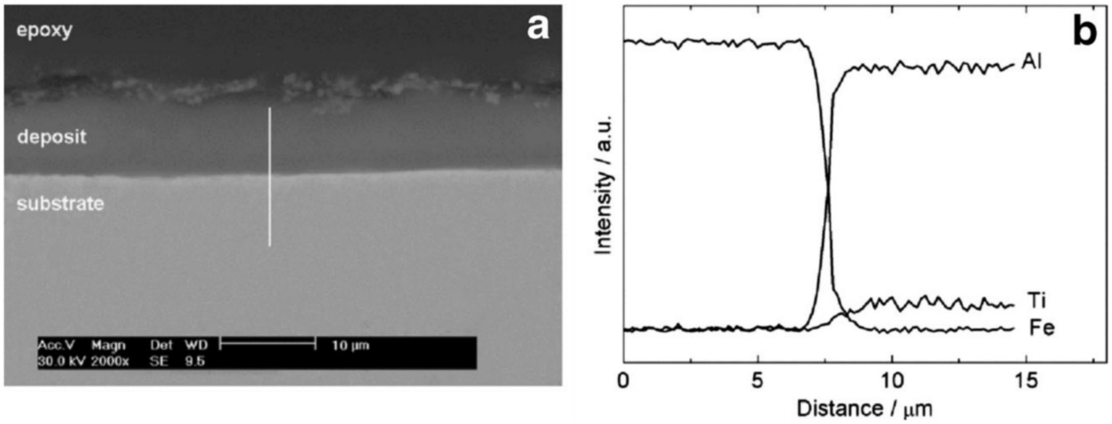

Figure 3: The cross-sectional image (**a**) and EDS line scans (**b**) of a typical Al-Ti alloy layer, $Al_{91.9}Ti_{8.1}$, prepared in $AlCl_3$-BMIC ionic liquid containing 0.22 mol L^{-1} $TiCl_4$ at 1 mA cm^{-2} (30).

3. Challenges and Perspectives

In this review, we show the progress of the electrochemical behavior of titanium ions in RTILs. The results show that the titanium alloys, mainly Ti-Al, Ti-Zn alloys, could be obtained with RTILs by electrolysis method through alloying contribution of substrate or co-deposition process. However, it is difficult to get pure titanium metal in RTILs, and many researchers claim that it is impossible to prepare metallic titanium in RTILs by electrolysis. Only a few scholars reported that they successfully got pure titanium plating or wires with less than 10 nm thickness or less than 100 nm length, respectively. Those plating or wires are so small that this method is not promising in the electroplating and titanium extraction industry.

The primary reason for hindering pure titanium production in RTILs is that titanium element has many oxidation states, and their reduction process is very complex. In general, the reduction steps of Ti $^{4+}$ in RTILs mainly relates to two steps, including Ti^{4+} to Ti^{3+} (or Ti^{2+}) and Ti^{3+} (or Ti^{2+}) to Ti. However, the solubility of Ti^{3+} or Ti^{2+} ions is very low, and, therefore, the precipitate compounds containing Ti^{3+} or Ti^{2+} will adhere to the surface of the cathode during the electrolysis process, which will further inhibit the reduction of titanium ions. To address this challenge, there are two strategies. The first pathway is to develop the new RTILs with high solubility to Ti^{3+} or Ti^{2+} ions. The second way is to adjust the reduction process of Ti^{4+} ions to avoid the generation of the precipitate compounds by the selection of additives or cathodic substrates.

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