

Effect of Electrodes and Salts Impurity on the Cyclic Voltammetry in Molten Li₂O/LiCl

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INTRODUCTION

Titanium and its alloys are advanced metallic materials for various industrial, astronautic and biomedical applications, because of their desirable properties of relatively low density, good fatigue strength and formability, and corrosion resistant. ¹ TiO₂ is also used as a non-radioactive surrogate for UO₂ in reduction studies. Titanium metal is conventionally produced from the Kroll process, ² which requires high energy input and inevitably releases hazardous gases such as chlorine. Electrolytic reduction of TiO₂ to titanium is promising and covers the shortages of Kroll process. Fray - Farthing - Chen (FFC) - Cambridge process is the first electrochemical method of TiO₂ reduction in molten CaO/CaCl₂ at 850 – 950 °C with Ca²⁺.^{3,4} Other than FFC process, the calciothermic reduction is another electrochemical method in CaO/CaCl₂ salt, reduction TiO₂ with metallic calcium. ⁵ Instead of using molten calcium salts at high temperatures, Li₂O/LiCl is used as the electrolyte in TiO₂ electrolytic reduction at a much lower operation temperature at 650°C. ^{6,7}

Cyclic voltammetry (CV), which can sweep in a wide potential range, is applied in TiO₂ reduction process at various potentials using TiO₂ as the cathode. A series of CVs of TiO₂ in 1w.t. % Li₂O/LiCl molten salt were measured and a sharp reduction current was found at -0.65V (vs. LiPb) which was assigned as the formation of LiTiO₂. ⁶ But there were no other peaks for further reduction. In molten calcium salt, CVs were also measured and multiple new peaks were observed. ⁸ By taken samples at each current peak, it was found that intermediates CaTiO₃ was involved and TiO₂ was gradually reduced to TiO through Ti₃O₅ and Ti₂O₃.

Other than watching reactions at varying potentials, experiment parameters like electrode materials and reduction potentials in this study also need to be determined through CV measurements. In order to find proper materials for cathode and anode for TiO₂ electrolytic reduction, and to determine electrolyte properties, CVs were measured in Li₂O/LiCl at 650 °C.

EXPERIMENTAL

Commercial lithium chloride (Alfa Aesar 13684) was used as electrolyte for the study. Lithium oxide (Alfa Aesar 41832) was added to LiCl to prepare a system with 0~1 w.t. % of Li₂O concentration in LiCl.

Three-electrode electrochemical system was used in electrolysis study, consisting of a working electrode (W.E.), a Ni/NiO reference electrode and a counter electrode (C.E.). The electrolysis cell was installed in a glovebox with argon atmosphere. The electrolyte is 150.00g LiCl mixed with Li₂O. A Kerrlab electric furnace was used for high temperature control. VersaSTAT 4 Potentiostat (Princeton Applied Research) and Versa Studio was used for the electrolysis control and data acquisition.

Cyclic voltammetry of Li₂O/LiCl molten salts were measured at 650 °C at scanning rate 20 mV/s. Stainless steel wire and Pt-Ir (Pt:Ir=9:1) wire are materials for working electrode. Materials for counter electrode are Pt-Ir wire and glassy carbon crucible (HTW GAZ 30) container. A new electrode bundle was prepared and used in measuring CVs of salts before and after reductions. The baseline of CV curves was considered at zero current, and the salt cathodic decomposition potential was the intersection of CV edge with the baseline.

RESULTS

Determination of electrodes materials

CVs of molten LiCl were measured with a Ni/NiO reference electrode, a stainless steel or Pt-Ir working electrode, and a Pt-Ir or glassy carbon counter electrode to test the performance of the electrode materials.

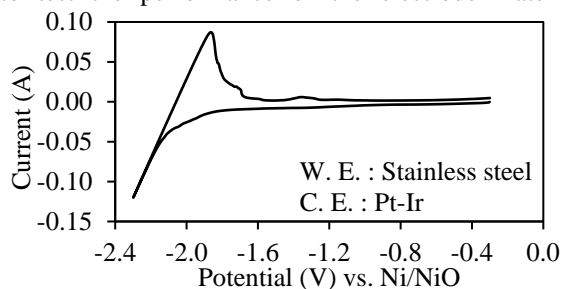


Fig. 1. CV of LiCl with stainless steel working electrode and Pt-Ir counter electrode

CV of salt with a stainless steel working electrode and a Pt-Ir counter electrode was shown in Fig. 1. The cathodic CV shows a clear edge and the decomposition potential was -2.06V . When cathodic potential was applied on working electrode, an anodic potential response was on the counter electrode to keep an electrolytic balance in electrolyte. As a consequence, as high as $+2.35\text{V}$ is balanced on the Pt-Ir anode. After repeating CV measurements with stainless steel cathode and Pt-Ir anode, the electrode was broken at the surface of electrolyte for the reason that Pt dissolves at $+1.65\text{V}$.⁹ Therefore, in TiO_2 reduction at a reduction potential higher than -1.65V , stainless steel is good for the experiment but Pt is not recommended as the anode. And glassy carbon was tested in the following CV measurements.

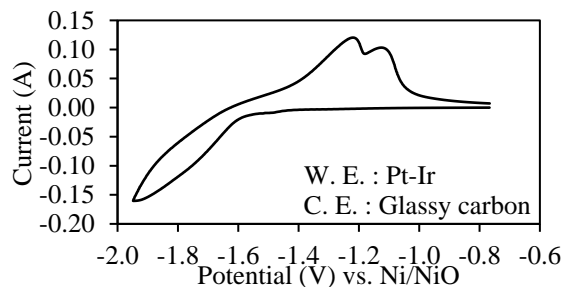


Fig. 2. CV of LiCl with Pt-Ir working electrode and glassy carbon crucible counter electrode

Pt-Ir was used as a working electrode and glassy carbon crucible as a counter electrode for CV measurement (Fig. 2). The reduction peak is wide and not reversible. Also, two peaks for Li metal re-oxidation reaction were observed, indicating one type of reaction on each metal component of cathode material. The CV curve is repeatable and the glassy carbon crucible is stable during the measurement. In conclusion, alloy materials like Pt-Ir is not good for cathode while glassy carbon crucible is a good candidate for anode in TiO_2 reductions.

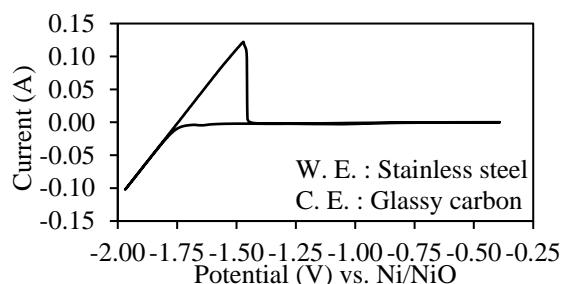


Fig. 3. CV of LiCl with stainless steel working electrode and glassy carbon crucible counter electrode

Based on previous CV measurement in Fig.1 and 2, it is determined that the stainless steel wire works as the

working electrode and the glassy carbon crucible as the counter electrode. CV of salt was measured with this collocation (Fig. 3) to verify the electrodes are proper for the reduction. It can be determined that the cathodic decomposition potential is -1.75V using this specific Ni/NiO reference electrode. Therefore, based on clear and repeatable CV curves, stainless steel cathode and glassy carbon anode are stable during the study, and are proper electrodes for TiO_2 reductions.

Study on properties of salts

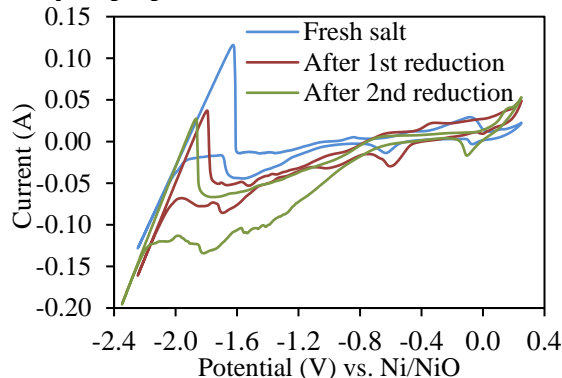
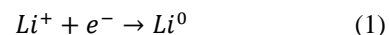


Fig. 4. CVs of 1 wt. % $\text{Li}_2\text{O}/\text{LiCl}$ with stainless steel working electrode and glassy carbon crucible as counter electrode before and after TiO_2 reduction

Fig. 4 shows CV measurements before and after TiO_2 reductions. The reduction was carried out at -0.3V vs. Li^+/Li with 150% of theoretical charge, and again under the same conditions in used salt.

For fresh salt, the cathodic decomposition potential is determined as -1.93V vs. Ni/NiO when reaction (1) takes place. Then, the reduction was done based on this decomposition potential using this specific Ni/NiO reference electrode.



After TiO_2 reductions, CVs showed huge reduction peaks from -0.8V and the peak becomes bigger after the second reduction. Shapes are different for CVs before and after reduction, indicating a more complicated composition with impurities. In conclusion, lithium salt after TiO_2 reductions becomes more complicated with impurities, so it is not recommended to be reused.

CONCLUSION

Cyclic voltammetry measurements were taken to compare electrode materials and .By measuring CVs using different electrodes, it can be determined that stainless steel wire and glassy carbon crucible were proper materials for cathode and anode in current study, respectively. Lithium salt after TiO_2 reduction is not reusable, based on comparison among CV measurements for molten salts before and after reductions.

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