



A PRS model for accurate prediction of the optimal solid oxide cathode structure for the preparation of metals in molten chlorides

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ABSTRACT

A theoretical model correlating the precursor porosity, P (in volume percentage), the metal-to-oxide molar volume ratio, R , and the cathode volume shrinkage S (in volume fraction, experimentally determined) (the PRS model) with the deoxidation speed of the solid metal oxide cathode in molten chlorides has been developed, allowing accurate prediction of the optimal cathode porosity by a simple equation, $P_{\text{opt}} = \frac{3R + S - 1}{3R} \times 100\%$.

Tests of this equation in practices suggest P_{opt} to be an intrinsic parameter to the oxide. For example, the predicted values of P_{opt} for the electrolysis of TiO_2 and Ta_2O_5 cathodes are about 67% and 25% respectively, and a cathode porosity far away from P_{opt} would suppress the deoxidation seriously. The established model has been well verified by the electrolysis of the oxides of Si, Ti and Ta.

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1. Introduction

Most of traditional metallurgical processes are both energy and pollution intensive, resulting in many unaffordable but widely demanded metals in the society today, such as titanium, despite they are actually rich in natural resources. The recent invention [1] of direct electrolysis of solid compound (oxide or sulfide) cathode against a graphite anode in molten chlorides, potentially to be low in both energy consumption and environmental footprint, has stimulated worldwide research aiming to prepare many important metals and alloys such as Ti, Si and Ta [1–5]. However at the present stage, it seems that both the electrolysis speed and current efficiency of this process need to be further improved before the industrial scale-up, particularly for the production of Ti [6–8]. As fast electrolysis is essential for high current efficiency [8–10], there is an urgent demand for a more fundamental insight into the rate-determining mechanism of the solid cathode process.

In view of element balance, the electro-reduction of a solid metal oxide generally includes the departure of the O^{2-} ion from the cathode, the transfer of O^{2-} through the molten salt, and the discharge of O^{2-} to a gaseous product on the anode. Therefore, although the detailed reaction mechanism from the oxide to the metal might be complicated as focused by most of the published researches [6–16], the

net overall cathode process is simple, i.e., the removal of oxygen from the cathode. However, up till now, the overall mass transfer dynamics for oxygen removal from the cathode is far away from well established.

There has been a perception that the intrinsically slow solid state diffusion of O in the oxide and/or the generated metal plays a decisive role in the deoxidation of a solid cathode [1,2,17,18], and setting of very long electrolysis times was common for various metal oxides [1–16]. However, direct electro-deoxidation of oxide pellet could proceed initially at the current collector/metal oxide/electrolyte three-phase interlines (3PIs), generating a porous metal coating on the unreduced oxide even for a dense precursor [19–21]. Since the electrolyte may enter the pores automatically, the generated porous metal layer not only can serve as the electron conducting medium, but also provide effective liquid state channels for the outward diffusion of O^{2-} . In other words, new metal/metal oxide/electrolyte 3PIs may form and the inward propagation of the dynamic 3PIs leads to the bulk reduction of oxide cathode (Fig. 1a). In this manner, only the solution diffusion of O^{2-} needs to be considered for the oxygen transfer inside the cathode [21]. However, since the solution diffusion coefficient of O^{2-} in the electrolyte is about 10^{6-8} times higher than that of O in most solid oxides and metals [18], it is preferred to ensure unobstructed solution diffusion channels inside the cathode to ensure fast electrolysis [8].

In this communication, a new O^{2-} diffusion model correlating the precursor cathode porosity, P , the metal-to-oxide molar volume ratio, R , and the cathode volume shrinkage, S , has been developed. With this PRS model, both the deoxidation speed and the intrinsic optimal

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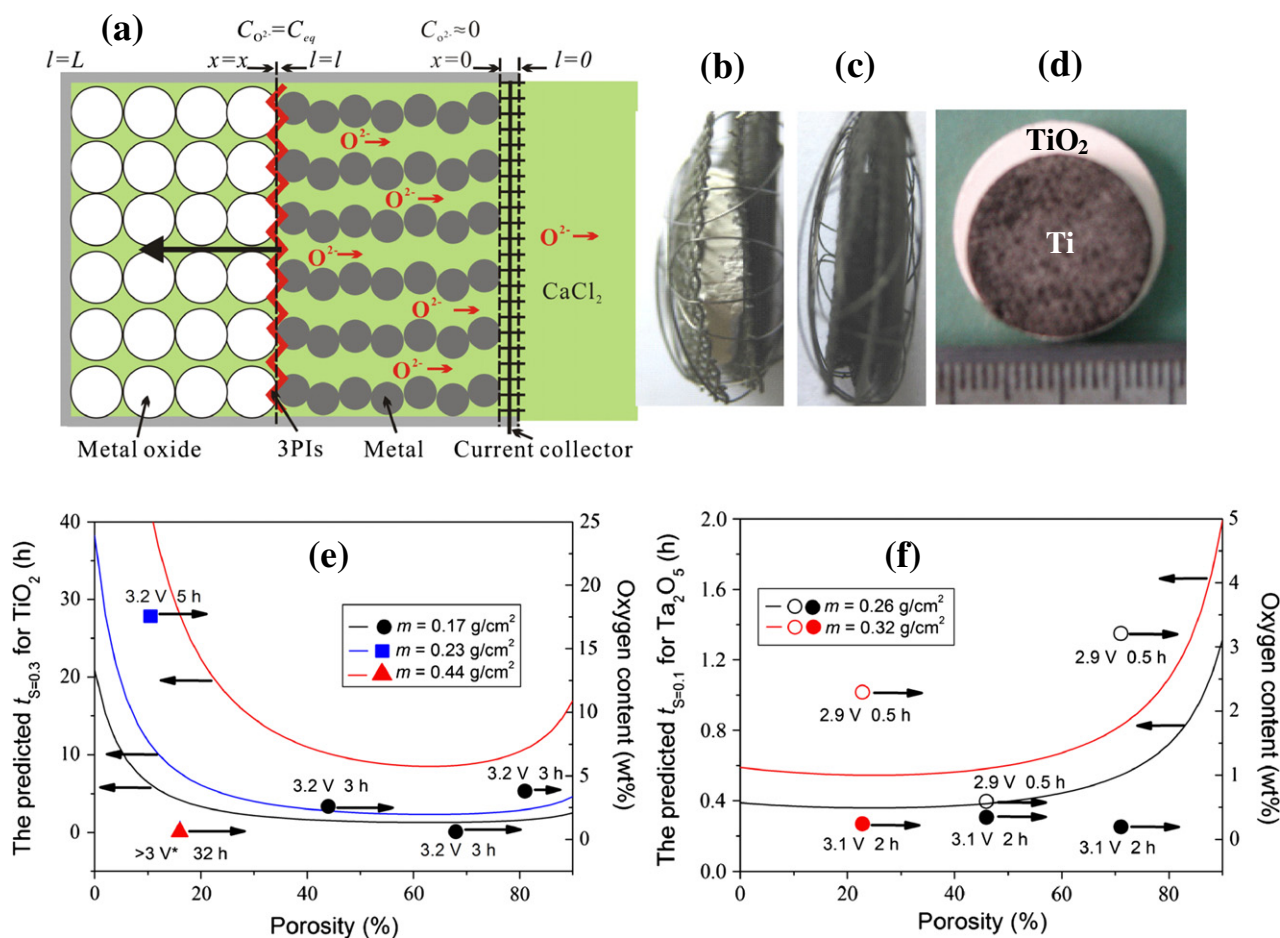


Fig. 1. (a) Schematic liquid oxygen ions diffusion model for the electrolysis of solid oxide cathode. l is the reduced thickness of the oxide pellet and x is the thickness of the generated porous metal (diffusion layer); (b) side views of a TiO_2 pellet cathode (~68% porosity) wrapped by Mo meshes and wires; (c) the cathode after electrolysis; (d) front views of the pellets in (b) and (c) respectively; (e, f) plots (solid lines) of the PRS model predicted deoxidation time (left vertical axis) of TiO_2 (e) and Ta_2O_5 (f) precursors with indicated mass loadings against the precursor porosity. The oxygen contents (right side vertical axis) measured in the electrolytic products from TiO_2 (e) and Ta_2O_5 (f) cathodes with indicated mass loading are also superimposed against their porosities (the electrolysis cell voltage and time are indicated next to scattered data symbols). The experimental data for TiO_2 were derived from Ref. [8] except for the filled red triangle in (e) which was from Ref. [16] (* the applied cathode potential was comparable to other electrolyses at 3.2 V [7,10,16]); the experimental data in (f) for Ta_2O_5 were measured in this work.

cathode porosity of a given oxide for the fastest deoxidation can be accurately predicted.

2. Theoretical model

Fig. 1a shows schematically the O^{2-} transfer model. It is assumed that (1) the precursor, the possible intermediates and the final metallic product are all in solid state, (2) a sufficient overpotential can be imposed to the cathode so that the oxide or any intermediate near the 3PIs can be reduced to the metal and O^{2-} quickly, and (3) the outward diffusion of O^{2-} through the generated porous metal layer becomes the rate-determining step. Thereof, the concentration of O^{2-} near the 3PIs can be the equilibrium concentration C_{eq} of the cathode reaction ($\text{MO}_z + 2ze = \text{M} + z\text{O}^{2-}$). C_{eq} would increase with the overpotential according to the Nernst equation until it reaches at the maximum or saturation concentration C_{sat} of the O^{2-} in the electrolyte.

Assuming that $D_{\text{O}^{2-}}$ is the diffusion coefficient of the oxygen ions in bulk electrolyte, then, at thickness x , the maximum diffusion flux (J , mol/s) of O^{2-} across the apparent cathode area A is,

$$J = A \frac{D_{\text{O}^{2-}} P_m C_{\text{eq}}}{f x} \quad (1)$$

In which, P_m is the porosity of the generated porous metal and f is the tortuosity coefficient of the pores. For an oxide (MO_z , with density ρ_o , formula weight M_o) cathode with porosity P_o , the amount of oxygen dN (mol) in the pellet with thickness dl need to be removed is

$$dN = z\rho_o(1-P_o)Adl/M_o. \quad (2)$$

Considering the possible volume shrinkage of the cathode due to the sintering of the generated metal, such as Ti (Fig. 1b–d) [8,15,16], the reduced thickness l of the oxide pellet might be larger than the thickness of the generated porous metal x (diffusion layer), as shown in Fig. 1a. Denoting the variable S as the volume shrinkage ($0 \leq S < 1$, $S=0$ indicates no shrinkage) and considering uniform shrinkage in each of the three dimensions, it can be derived that $x = (1-S)^{1/3}l$. Since $dN = Jdt$, there is

$$\frac{z\rho_o(1-P_o)}{M_o} dl = \frac{D_{\text{O}^{2-}} P_m C_{\text{eq}}}{(1-S)^{1/3} f} dt. \quad (3)$$

Defining V_o^* and V_m^* as the molar volumes of the oxide (with the common formula, MO_z) and the metal respectively, both are constants with their ratio $R = V_m^*/V_o^*$. In the oxide cathode, a mole of

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