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Letter

Environmental and energy gains from using molten magnesium–sodium–potassium chlorides for electro-metallisation of refractory metal oxides

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Abstract

The molten eutectic mixture of magnesium, sodium and potassium chlorides ($MgCl_2$–NaCl–KCl) has inappreciable solubility for oxide ions, and can help disengage a carbon anode from the oxide ions generated at a metal oxide cathode, and effectively avoid carbon dioxide formation. This “disengaging strategy” was successfully demonstrated in electro-reduction of solid oxides of zirconium and tantalum. It has led to significantly higher current efficiency (93%), and lower energy consumption (1.4 kW h kg^{-1}) in electrolysis of tantalum oxide to tantalum metal compared to the conventional electrolysis in molten calcium chloride (*e.g.* 78% and 2.4 kW h/kg-Ta).

Keywords: Electrometallisation; Molten salt; Tantalum; Electro-reduction; Magnesium chloride

1. Introduction

Refractory metals play crucial roles in our materials based modern civilisation [1]. Industrial production of refractory metals is commonly achieved *via* the pyrometallurgical process that is often carbon and/or energy intensive. It also involves multiple steps, such as electrolytic production of an alkali or alkaline earth metal that is then used to reduce a refractory metal compound to the metal at elevated temperatures. The compound, *e.g.* K_2TaF_7 or $ZrCl_4$, is obtained from the mineral *via* complex extraction, conversion and purification chemistry. Alternatively, refractory metal extraction can be achieved by electrolysis of metal oxides in molten salts with high diffusivity for O^{2-} ions which can then transport to, and discharge at the anode [2,3]. This mechanism would be ideal if coupled with an inert [4–7], or an oxide ion conductor anode [7,8], to produce the O_2 gas, which is yet pending for commercial verification. Thus, similar to electrolysis of Al_2O_3 dissolved in cryolite based molten fluorides, carbon anodes are still the choice in electro-reduction of solid metal oxides (*e.g.* TiO_2, ZrO_2 and Ta_2O_5) in calcium containing molten chlorides, leading to CO_2 emission [9–12]. In addition to the environmental impact, anodic formation of CO_2 causes challenging technical problems, such as carbon contamination of products, low current and energy efficiencies, and process interruption due to anode consumption.

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Herein, we propose a "disengaging strategy" in which $MgCl_2$ based molten salts with low O^{2-} solubility are used so that the O^{2-} ion generated at the oxide cathode cannot transport to and discharge at a carbon anode, but is converted to MgO which precipitates out of the molten salt. The anode reaction is thus changed to oxidation of the Cl^- ion to the Cl_2 gas, which makes the carbon anode effectively non-consumable, eliminating CO_2 emission and all the related problems. The Cl_2 gas generated in this new process is corrosive and cannot be directly emitted to the atmosphere. However, it is a valuable and widely used chemical for many traditional and new applications, especially in the H_2–Cl_2 fuel cell for generation of electricity and the HCl gas which is needed to convert MgO back to $MgCl_2$ [13]. Thus, the combination with the H_2–Cl_2 cell can close the process to maximise efficiency and minimise waste and emission.

2. Experimental

Anhydrous $MgCl_2$, NaCl, and KCl (analytical grade, Tianjin Guangfu Fine Chemical Research Institute, or Sinopharm Chemical Reagent Co., Ltd, China) were mixed in the eutectic ratio (5:3:2 in mole ratio and 5 mol in total amount), and heated in a graphite or alumina crucible (inner diameter: 25–50 mm; height: 200–700 mm) in a programmable vertical furnace equipped with a sealable stainless steel retort (Wuhan Experimental Furnace Plant). The furnace temperature was slowly raised to and maintained at 400 °C for more than 12 h, and then to 700 °C until the salt mixture was fully molten. Pre-electrolysis of the molten salt was applied at 1.6 V to remove moisture and other redox-active impurities with the graphite crucible (or a graphite rod of 10 mm diameter in the alumina crucible) as the anode and a molybdenum (Mo) wire (diameter: 2 mm) as the cathode. Pre-electrolysis lasted (*ca.* 10 h) until the current reached a low and stable background level.

Powders of ZrO_2 and Ta_2O_5 (analytical grade; particle sizes: 300 nm; Zhuzhou Cemented Carbide Works Imp. & Exp. Company) were individually die-pressed into cylindrical pellets (10 MPa, 13 or 20 mm in diameter, 1.1–1.7 mm in thickness, 0.3–2.0 g in weight), sintered in air at 1000 °C for 2 h, and sandwiched between two Mo meshes to form an assembled cathode. Electrolysis of metal oxides was performed at 2.0–2.4 V in the above mentioned eutectic melt at 700 °C under argon. After electrolysis for a designated time, the cathode was removed from the furnace, cooled in argon, washed in distilled water, or in dilute HCl (0.1 mol L^{-1}) and water again, and then dried in vacuum at 80 °C before further analyses. The products were characterised by X-ray diffraction spectroscopy (X-ray 6000 with Cu Kα1 radiation at $\lambda = 1.5405$ Å, Shimadzu, Japan), transmission electron microscopy (TEM, JEM-2010, Japan), and FEI Sirion Field Emission Gun SEM system equipped with an EDAX GENESIS 7000(EDX).

3. Results and discussion

Apart from having low solubility for the O^{2-} ion, $MgCl_2$ is selected because MgO has a molar volume (11.20 cm^3 mol^{-1}) smaller than many other oxides (*e.g.* 21.69 and 26.95 cm^3 mol^{-1} for ZrO_2, and $TaO_{2.5}$, respectively). Thus, if MgO is precipitated inside an oxide cathode with sufficient porosity ($>40\%$ and 30% for ZrO_2 and Ta_2O_5 respectively), it would not fully block the pores for ion passage. Thermodynamically, most oxides of transition metals can be reduced to the respective metals in molten $MgCl_2$ by this strategy (Table 1). A drawback of molten $MgCl_2$ is its relatively high vapour pressure (1.03 kPa, 750 °C), which causes loss of molten salt and safety risk. Thus, it is better used together with other chloride salts, such as NaCl and KCl. Individually, $MgCl_2$, NaCl, and KCl all have relatively low solubility for their oxide counterparts (<600 ppm in molten $MgCl_2$ at 730 °C) [14,15], in contrast with $CaCl_2$ (>20 mol% at 850 °C) and LiCl (>10 mol% at 650 °C) [16,17]. Thus, the mixture of $MgCl_2$–NaCl–KCl (MNK) is expected to have low O^{2-} solubility, and transport of the O^{2-} ion in the mixed melt can be reasonably assumed to be insignificant.

The reduction of metal oxide in eutectic MNK (mole ratio: 5:3:2) is expected to form MgO precipitate in cathode. Ta_2O_5 and ZrO_2 were selected for demonstration. Note that ZrO_2 is the most stable oxide (or most difficult to reduce) in comparison with the others listed in Table 1. The Ta_2O_5 (1.0 g) and ZrO_2 (0.2 g) pellets were electrolyzed at a cell voltage of 2.0 V and 2.4 V against a graphite anode for 4.5 h and 6.7 h, respectively. The XRD pattern of the product presented the metal and MgO if they are washed with water, or the metal only if pickled in dilute HCl (0.1 mol L^{-1}) first and then rinsed in water, as shown in Fig. 1a–c.

Obviously, these XRD findings are strong evidence that the electro-reduction generated O^{2-} ion indeed reacted with the Mg^{2+} ion to form insoluble MgO in the cathode. In agreement with this attribution, in all experiments of this work, insignificant erosion was seen on the graphite anode after electrolysis as evidenced by the two photographs in Fig. 2a. In these photographs, it can been seen that the fine spiral machining marks on the side wall of the graphite rod remained clearly intact after electrolysis for *ca.* 100 h, even though these protruding parts are usually the most vulnerable sites to chemical or electrochemical attack. It is well-known that

Table 1
Standard decomposition voltages of metal oxides in molten $MgCl_2$ at 700 °C.

Cell reactions	Decomposition voltage (V)
$MgCl_2 = Mg + Cl_2(g)$	2.614
$2MgCl_2 + ZrO_2 = Zr + 2MgO + 2Cl_2(g)$	2.331
$2MgCl_2 + TiO_2 = Ti + 2MgO + 2Cl_2(g)$	1.949
$2MgCl_2 + SiO_2 = Si + 2MgO + 2Cl_2(g)$	1.865
$5MgCl_2 + Ta_2O_5 = 2Ta + 5MgO + 5Cl_2(g)$	1.638
$5MgCl_2 + Nb_2O_5 = 2Nb + 5MgO + 5Cl_2(g)$	1.488
$3MgCl_2 + Fe_2O_3 = 2Fe + 3MgO + 3Cl_2(g)$	0.939
$MgCl_2 + NiO = Ni + MgO + Cl_2(g)$	0.743

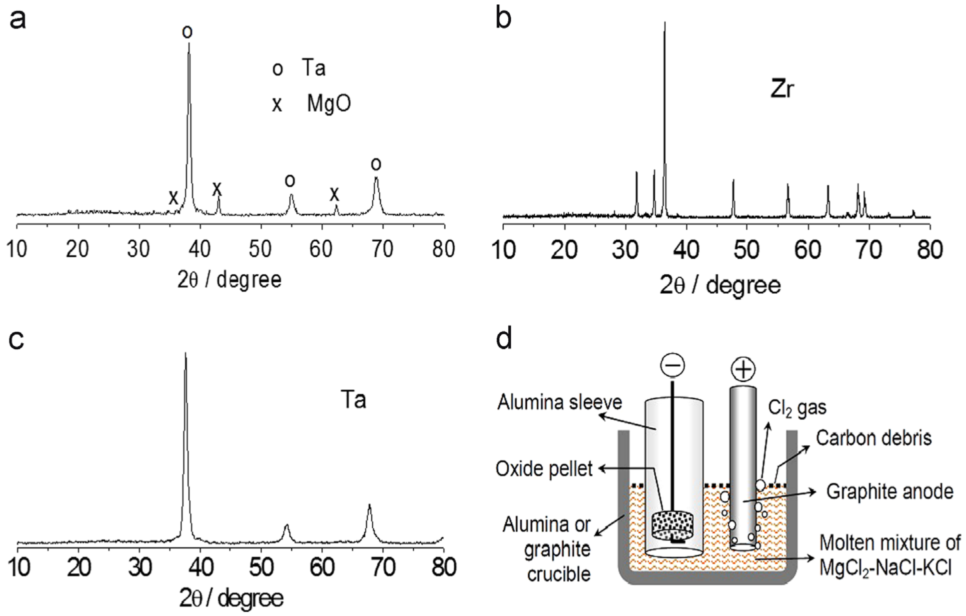

Fig. 1. (a–c) XRD patterns of products from electrolysis of metal oxides (on cathode) in eutectic MNK at 700 °C: (a) 1.0 g, Ta_2O_5, 2.0 V, 4.5 h, water washing; (b) 0.2 g ZrO_2, 2.4 V, 6.7 h, dilute HCl and water washing; (c) 1.0 g, Ta_2O_5, 2.0 V, 4.5 h, dilute HCl and water washing. (d) Illustration of the electrolysis cell.

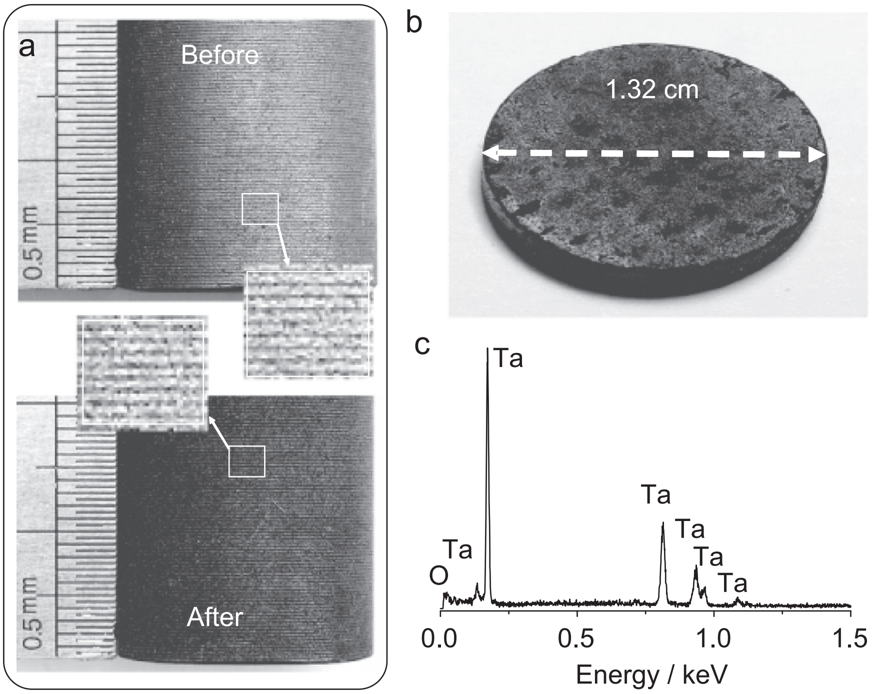

Fig. 2. (a) Graphite rod anode (dia. 2.0 cm) before and after repeated electrolysis experiments for *ca.* 100 h in the eutectic MNK melt. The enlarged boxes show the spiral marks on the side wall of the graphite rod. (b) Ta_2O_5 pellet collected after electrolysis in molten MNK (c) EDX of Ta powder produced by electrolysis of Ta_2O_5 (1.0 g, 2.0 V, 700 °C).

erosion on a graphite anode can be serious if the anode reaction is the discharge of the O^{2-} ion in $CaCl_2$.

After reduction, the original white Ta_2O_5 pellet turned black (Fig. 2b) and the XRD pattern of the product showed Ta and MgO. It is interesting that the precipitation of MgO in the pellet did not destroy it, but the pellet became even stronger thus could be easily handled. After HCl and water washing, fine powders were finally collected, and EDX analysis indicated that the product consisted of mainly Ta, in line with the XRD result. The only other element in the product detected by EDX was O with a very small peak. This is common for pure metal particles since EDX signal mainly comes from the surface layer and metal particles often have a oxide coating [9,10].

The effect of MgO accumulation in the Ta_2O_5 cathode was insignificant on electro-reduction of the oxide to a phase pure metal, although the 50% porosity oxide pellets were similar to

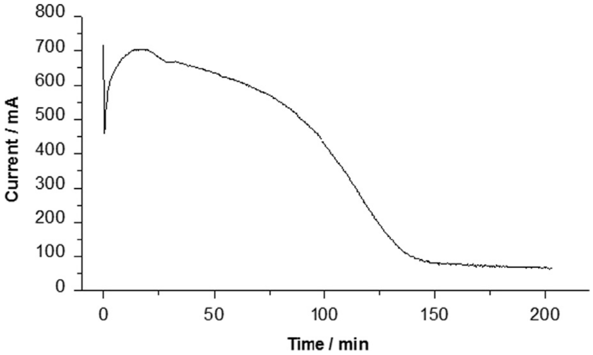

Fig. 3. Current-time plot of electro-reduction of a pellet of 1.7 g Ta_2O_5 in MNK at 2.0 V and 700 °C.

those commonly used for electro-reduction in molten $CaCl_2$ [18–23]. As shown in Fig. 3, the 1.7 g pellet could be fully reduced in a short time (~2.5 h). This could be due to that the 50% porosity was still much higher than 30% when the ion passages in a Ta_2O_5 cathode may be fully blocked by the precipitated MgO, so the liquid transfer has not been a problem.

The most promising result from electrolysis of metal oxides in molten MNK is the lower voltages and temperatures applied to achieve full reduction. This advantage can be mainly attributed to the anodic discharge of the Cl^- ion in MNK, which eliminates various polarisations caused by diffusion and anodic discharge of the O^{2-} ion as mentioned before. For electro-reduction of Ta_2O_5 in MNK, the current efficiency (CE) could be as high as 93%, and the energy consumption (CE) lower than 1.4 kW h/kg-Ta. These data are much improved from the best results reported in the literatures so far, *e.g.*, 78% and 2.4 kW h/kg-Ta with similar oxygen contents [9]. For electrolysis of the ZrO_2 pellet at 2.4 V, the CE was *ca.* 39%, corresponding to an EC of 7.1 kW h/kg-Zr. The relatively low CE for ZrO_2 may be due to the applied cell voltage being too close to the theoretical decomposition voltages of ZrO_2 (2.33 V) and the molten salt (*cf.* Table 1), leading to slower reduction, longer electrolysis time, and hence more side reactions. Nontheless, the results of this work are still better than those reported for electrolysis of ZrO_2 in molten $CaCl_2$ at 850 °C in a graphite crucible, *e.g.* 35.4% and 10.5 kW h/kg-Zr [24].

4. Conclusions

In summary, we have demonstrated experimentally the principle and feasibility of using the molten eutectic mixture of $MgCl_2$–NaCl–KCl to disengage O^{2-} from transporting to, and discharging at a graphite anode, and hence eliminate CO_2 emission in electro-reduction of solid metal oxides to the respective metals. In comparison with previous studies in molten $CaCl_2$, results from this work also show that this “disengaging strategy” brings about other benefits, such as quicker reduction and lower energy consumption. These preliminary findings shall encorage further study of the “disengaging strategy” as an enivronment-friendly and energy efficient methode for refractory metal extraction.

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