



Production of Fine Tungsten Powder by Electrolytic Reduction of Solid CaWO_4 in Molten Salt

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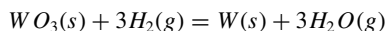
Direct electrochemical reduction of solid CaWO_4 to fine W powder in molten CaCl_2 -NaCl was studied by cyclic voltammetric measurement and potentiostatic/constant-voltage electrolysis. The effect of electrolysis conditions such as electrolysis time, temperature and voltage on the quality of the product (the residual amount of CaWO_4) was systematically investigated. Based on the solubility tests of CaWO_4 in the melt in a wide temperature range, an unprecedented strategy on electrolytic extraction of pure tungsten powder was proposed and confirmed, which involves low-temperature and short-duration electrolysis of solid CaWO_4 in molten CaCl_2 -NaCl eutectic salt (1023 K, 10-hour electrolysis) followed by a simple washing process in the same melt at a higher temperature (1123 K, 1-hour washing). The particle size of the as-prepared W powder is less than 200 nm. This process exhibits a high yield and increased energy efficiency for production of fine W powder from CaWO_4 .

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Tungsten, which possesses a high melting point (3695 K) and excellent mechanical properties, has been widely applied in mining, metallurgy, machinery, construction, armament industry and etc.¹ Generally, there are two kinds of tungsten ores consist in the earth crust, i.e. wolframite ((Fe/Mn) WO_4) and scheelite (CaWO_4), with a rough ratio of 30:70. At present, a great majority of industrial tungsten is produced from feedstock of wolframite despite its relatively low abundance. Wolframite can be easily converted into tungsten trioxide *via* an alkaline dissolution process. Metallization is then fulfilled by heating the resulted tungsten trioxide with hydrogen. Although the reserve of scheelite is much higher than that of wolframite, the difficulties encountered in the alkaline dissolution process to transfer scheelite into tungsten trioxide severely restrict the widespread use of scheelite in tungsten extraction.² On the other hand, China accounts for about half of the tungsten resource and 83% of the worldwide production of tungsten metal.³ In response to the rapid exhaustion of wolframite reserves in recent years and to fully exploit the natural W-based resources, a sustainable tungsten extraction route is highly desired. In this sense, the development of new technology for producing tungsten from scheelite is needed.

Besides the forenamed problem of low utilization ratio of scheelite in industry, the main tungsten production method based on hydrogen reduction (as depicted in reaction 1)¹ has its inherent demerits.



$$(\Delta G = -1.901 \text{ kJ mol}^{-1}, \Delta H = 81.37 \text{ kJ mol}^{-1}, 1123 \text{ K}) \quad [1]$$

As a result of the endothermic nature of the reaction at 1123 K, extra large amounts of energy must be applied to sustain the reaction, which causes the high energy consumption and low energy efficiency of traditional tungsten extraction process. The above inconvenience then results in a market price of pure tungsten as high as \$20,075 per ton as of October 2008.⁴

Due to its high melting point, fabrication of tungsten products (rods, wires, tubes, plates, etc) and tungsten alloys is always through powder metallurgy (PM) process. The particle size and purity of tungsten powders are crucial to the PM process. According to the particle size equation (equation 2), the particle size of tungsten powder produced from hydrogen reduction method is 4.5~8.5 μm .² It is too big to meet the requirements for preparing high-performance tungsten-

based materials.⁵

$$\lg F = 3.54 + 0.33 \lg \rho - 1.9 \lg T + 0.28 \lg h + 0.002T + 0.028D \quad [2]$$

(F : particle size of tungsten powder, μm ; ρ : apparent density of WO_3 , g cm^{-3} ; T : reduction temperature, K; h : thickness of material layer, cm; D : particle size of WO_3 , μm)

Based on the findings that WO_3 is unstable in molten CaCl_2 and CaWO_4 is insoluble in molten CaCl_2 -NaCl at lower temperature, Karakaya et al. recently obtained fine tungsten powder *via* electrolytic reduction of solid CaWO_4 in CaCl_2 -NaCl salt at 873 K.⁶ Compared with other methods, this method directly utilizes solid CaWO_4 as raw material, which is capable of simplifying the production process and improving the utilization ratio of scheelite. However, electrolytic extraction of tungsten from CaWO_4 suffers from relatively sluggish electrode kinetics. Since the process is a direct solid-to-solid reaction,⁷ the speed of this reaction is slower than that of solid-to-liquid, solid-to-gas and others. To accelerate the reaction speed, high-temperature is required to conduct the electrolysis, such as extraction of Ti at 1123–1223 K.^{8,9} In addition, a high contact resistance exists in the electrolytic product consisting of less-interconnected fine tungsten particles (note that the extremely high melting point of tungsten makes its particles hardly to be sintered), which in turn causes a large iR drop across the cathodic material. The retarded effect of iR drop becomes severe when electro-reduction pathway reaches inner part of precursory pellets, causing the presence of unreduced CaWO_4 inside of pellets. In order to obtain pure product, a long reaction time is required to overcome the barrier originated from iR drop, resulting in a low current efficiency and high energy consumption.^{10,11} Normally, the electrode kinetics can be enhanced by elevating the temperature of the process for direct electro-reduction of solid compounds,⁷ but excessively elevated temperature will inevitably lead to severe dissolution of CaWO_4 in the melt and eventually cause a low yield. Therefore, the electrolytic extraction of W was reported to be more effective at a relative lower temperature of 873K.⁶ However, such a low reaction temperature is not optimized, yet. In this context, the electrolysis temperature and duration should be compromised to ensure a balance between fast electrode kinetics and an acceptable yield.

In present study, we propose an unprecedented strategy on electrolytic extraction of tungsten by utilizing low-temperature and short-duration electrolysis of solid CaWO_4 followed by a simple washing process in the same melt at a higher temperature. Along with solubility tests of CaWO_4 in molten salts, the correlation between electrolysis parameters (such as electrolysis time, temperature and voltage) and the residual CaWO_4 in the products have been systematically

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investigated, which proves the effectiveness of the proposed strategy on obtaining pure and fine tungsten powder *via* direct electrochemical reduction process in a more energy-saving manner.

Experimental

Experimental set-up, electrolyte and electrodes.— CaWO_4 powder (with purity higher than 99.9 wt%; purchased from Tianjin chemical reagent company and used as received) was die-pressed using a pressure of ~ 7 MPa, and then the preformed pellet (weight: 2.0–2.5 g; diameter: 20 mm; height: 1.8–2 mm) was annealed in air for 2 h at 923 K. The annealed pellet, which was first wrapped by foamed Ni film and was tightened using Mo wire, was used as cathode assembly in the electrolysis process. A eutectic CaCl_2 -NaCl (1:1 in molar ratio) was contained in an alumina crucible (inner diameter: 75 mm; height: 130 mm). The salt mixture was baked for 48 h at 523 K in an open electric furnace (Wuhan electric furnace company) to remove residual moisture. Following the drying process, the alumina crucible contained with the salt was then placed on the bottom of a stainless steel reactor which was placed in an electric furnace. The reactor was then heated to 1123 K at a ramp of 4 K min^{-1} under the protection of internal argon flow. The same ramp (4 K min^{-1}) was also used to decrease temperature to desired reaction temperatures. A two-electrode cell configuration was applied to both pre-electrolysis and electrolysis processes. A graphite rod (15 mm in diameter and 200 mm in length) connected to an iron rod (diameter: 5 mm) was employed as anode (the iron rod was kept away from the melt). The pre-electrolysis was performed for 4 h at a constant voltage of 2.7 V using foamed Ni film (about 35 mm \times 10 mm) which was attached to a Mo wire (diameter: 2 mm) as cathode. A schematic representation of similar electrochemical cell was previously illustrated in Reference 11 and 12.

Cyclic voltammograms (CVs) of CaWO_4 powder were recorded using a computer-controlled electrochemical system (CHI440A, Shanghai Chenhua, China). A CaWO_4 powder modified Mo electrode,¹² a graphite rod, and a home-made mullite-sheathed high temperature Ag/AgCl electrode were used as the working, counter, and reference electrode, respectively. Such a three-electrode configuration was also employed for the potentiostatic electrolysis of CaWO_4 pellets. All presented potentials in current study are reported with respect to the Ag/AgCl reference electrode.

Duration-dependent (0–24 h), temperature-dependent (873–1023 K) and voltage-dependent (2.2–3.1 V) electrolysis of CaWO_4 pellets were carried out in parallel. In some selected experimental runs, samples were cleaned by a molten salt washing process after electrolysis. The detailed washing steps were: (1) stopping electrolysis after it being carried out for 10 h, (2) rising molten-salt temperature to 1123 K at a rate of 5 K min^{-1} , (3) holding this temperature for 1 h, (4) lifting the sample above the molten salt, (5) after cooling in Ar atmosphere for 10 min, taking the sample out of the reactor. All samples were first washed using distilled water and then collected after centrifugal filtration and vacuum-dry at 323 K.

Solubility tests.— The solubility of CaWO_4 in molten CaCl_2 -NaCl at different temperature was measured by a series of static dissolution experiments. 873, 923, 973, 1023 and 1073 K were selected as the test temperature, respectively. During the test, CaWO_4 pellets were weighed and then wrapped by foamed Ni films and Mo wire. The initial weights of CaWO_4 pellets were denoted as A_s . The wrapped CaWO_4 pellets were immersed in the molten salt (weight: W_m) for 2 h at different temperatures (from low to high) and then taken out from the melt. After being cleaned by distilled water, the residual CaWO_4 was weighed again, and the weights were denoted as B_s . Correspondingly, the solubility (S_s) of CaWO_4 in the salt at different temperatures was calculated by following equation:

$$S_s = \frac{\sum_{i=1}^s (B_s - A_s)}{W_m} \times 100\% \quad [3]$$

Where $s = 1, 2, 3, 4, 5$, which is related to the temperature of 873, 923, 973, 1023 and 1073 K, respectively.

Materials characterization.— The dried products were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD tests were performed at room temperature (298 K) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA) with a graphite monochromator, and nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The scan rate was 4 degree min^{-1} . SEM analysis was performed on an FEI sirion field emission gun scanning electron microscope equipped with a CCD camera.

Results and Discussion

The solubility of CaWO_4 in molten CaCl_2 -NaCl eutectic salt.— Based on the phase diagram,¹³ the eutectic point of CaCl_2 - CaWO_4 is 1008 K with a composition of 95 mol% CaCl_2 and 5 mol% CaWO_4 . Considering the melting point of CaCl_2 (1057 K), it is impossible to extract tungsten through the solid-to-solid electrochemical reduction in pure molten CaCl_2 . The melting point of CaCl_2 -NaCl with a roughly equal molar ratio of CaCl_2 to NaCl is 780 K, making it a suitable electrolyte compatible with solid CaWO_4 . However, the solubility of CaWO_4 in the CaCl_2 -NaCl eutectic is unclear so far. In this work, the solubility of CaWO_4 in molten CaCl_2 -NaCl eutectic salt at different temperature was measured using the method described in section 2.2. The solubility-temperature curve is shown in Fig. 1. As can be seen, the solubility increases with temperature in the range between 873 and 1073 K. Below 1023 K, the solubility remains in small values less than 0.2 wt%. While a sharp increase of solubility appears when the temperature is increased from 1023 to 1073 K. The solubility changes from 0.2 wt% at 1023 K to 0.8 wt% at 1073 K. To ensure a predominant solid-to-solid reduction process, the electrolysis should be performed at a temperature not higher than 1023 K. To optimize the electrolysis temperature, electrolysis experiments were carried out at different temperatures in the range between 873 and 1023 K.

CV tests and electrolytic reduction of CaWO_4 pellet.— The SEM images of CaWO_4 pellet before and after electrolysis for 10 h at 3.1 V at 1023 K are given in Fig. 2. It is revealed that a steep decrease in particle size of the solid powder from ~ 1 micron (in precursor) to less than 200 nm (in product). Equation 2 indicates that the particle size of tungsten powder prepared *via* hydrogen reduction method is correlated with the particle size of precursory WO_3 , which means the employment of fine WO_3 feedstock is the prerequisite for the preparation of fine tungsten powder. In contrast to the traditional hydrogen reduction method, the direct electrolytic reduction of solid CaWO_4 is capable of producing ultra-fine tungsten powder from relatively larger tungsten oxide particles.

Given the fact that the molar volume of W (9.6 cm^3) is only $\sim 20\%$ of that of CaWO_4 (47.5 cm^3), it is conceivable that the

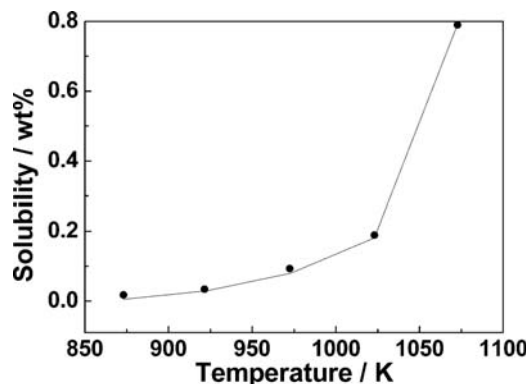


Figure 1. Solubility-temperature curve of CaWO_4 in molten CaCl_2 -NaCl eutectic.

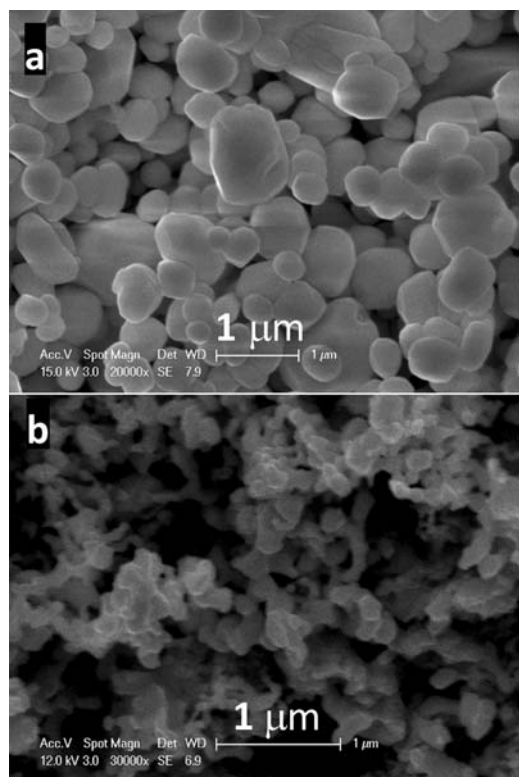


Figure 2. Typical SEM images of CaWO_4 pellet (a) before and (b) after electrolysis for 10 h at 3.1 V, 1023 K.

electro-reduction process will leave voids in the solid product while the agglomeration of the produced fine tungsten particles will be substantially retarded due to the extremely high melting point of tungsten. This synergetic effect will lead to the formation of ultrafine tungsten powder with diameter less than 200 nm. In fact, unlike the reduction of other metal oxides as described in previous investigations,^{12,14} in which an oxide pellet was transformed to an integrated metal or alloy pellet after electrolysis, it was found in this work that the CaWO_4 pellet was transformed to a pile of tungsten powder. The generation of less-interconnected tungsten powder is in agreement with the electro-generated Ta¹⁵ and Nb,¹⁶ which is believed to be a general phenomenon for electro-generated refractory metals or alloys.

To further elucidate the electro-reduction path of solid CaWO_4 , CV tests were carried out. Fig. 3a presents the first-cycle CVs of both bare Mo electrode and CaWO_4 modified Mo electrode recorded in molten $\text{CaCl}_2\text{-NaCl}$ at 1023 K. As can be seen, the onset potential of reduction appears at around -1.1 V with the formation of a current shoulder within the potential range between -1.1 and -1.8 V (notated as C1). At more negative potentials, large cathodic current forms at -2.0 V, resulting in the appearance of peak C2 located at -2.2 V. When further extending potential scan toward the negative potential limit, the electro-reduction and/or co-electro-reduction of cations in the melt bring about the formation of peak C3 which also emerges in the CV of bare Mo electrode.

Potentiostatic electrolysis of CaWO_4 pellet was then performed, aiming to specify the electro-reduction mechanism. The XRD patterns of electrolytic products obtained from potentiostatic electrolysis at -1.2 , -1.5 and -1.8 V are displayed in Fig. 3b. It is found that tungsten can be extracted at the above selected potentials with the presence of unreduced CaWO_4 . It is then rational to conclude that the formation of shoulder C1 is ascribed to the direct electro-reduction of solid CaWO_4 to solid tungsten. The electrolysis of CaWO_4 can be described by the following reactions:

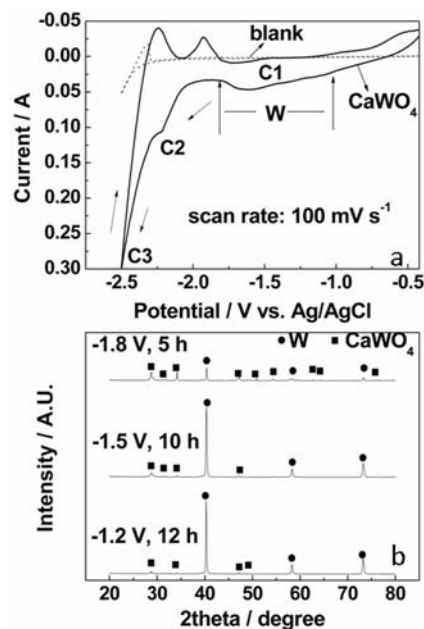
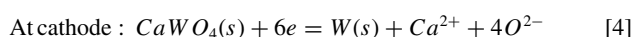
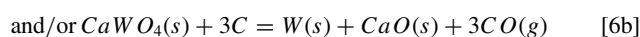
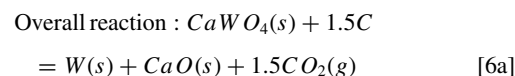
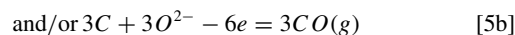
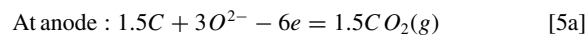


Figure 3. (a) first-cycle CVs of bare Mo electrode (dotted) and CaWO_4 modified Mo electrode (solid) recorded in molten $\text{CaCl}_2\text{-NaCl}$ at 1023 K; (b) XRD patterns of samples obtained from potentiostatic electrolysis of CaWO_4 pellets in molten $\text{CaCl}_2\text{-NaCl}$ at 1023 K at indicated conditions.



As depicted in the above reactions, the generation of solid tungsten is accompanied by the formation of CaO. It was reported that the saturation solubility of CaO in molten CaCl_2 at 1123 K is ~ 18.5 mol%.¹⁷ Although its solubility in currently used $\text{CaCl}_2\text{-NaCl}$ melts remains unspecified, it is rational to speculate that the formed CaO would dissolve into the melt until it is saturated with CaO under the experimental condition. Such in-situ generated CaO can be electro-reduced at potential more positive than that for salt decomposition, leading to the formation of peak C2 in the negative-direction potential scan.

The above results indicate that the electro-reduction of CaWO_4 to tungsten is a one-step reaction, implying that accurate control of electrolysis potentials is not compulsory for tungsten extraction. Therefore, constant-voltage electrolysis was utilized in the following experiments.

Temperature-dependent constant-voltage electrolysis.—To elucidate the influence of electrolysis temperature on the reduction rate, a series of electrolysis were carried out in parallel at 873, 973 and 1023 K using the same electrolysis duration (10 h) and voltage (3.1 V). The XRD patterns of the electrolytic products are displayed in Fig. 4a. It is obvious that more CaWO_4 was reduced to tungsten metal with rising electrolysis temperature, which means the reaction rate could be improved by increasing electrolysis temperature. This phenomenon well agreed with the common knowledge of the dependence of chemical reaction rate on temperature. Therefore, the reaction temperature was controlled at 1023 K for the following experiments.

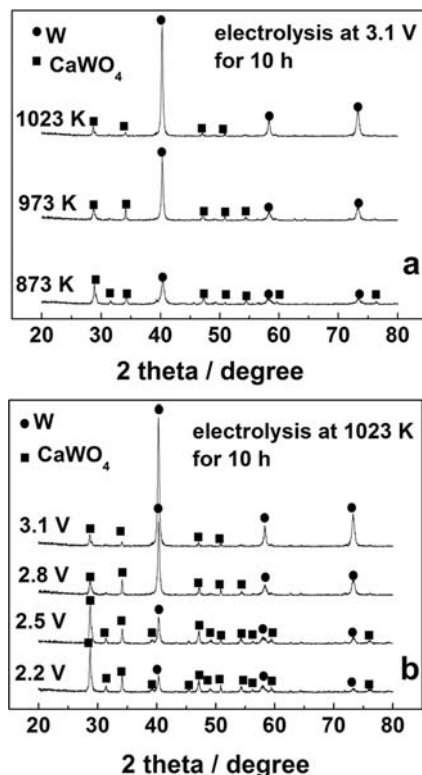


Figure 4. XRD patterns of samples obtained from (a) electrolysis at 3.1 V for 10 h at different temperatures and (b) electrolysis at 1023 K for 10 h under different cell voltages.

Voltage-dependent constant-voltage electrolysis.—According to the Gibbs free energy data at 1023 K, the decomposition voltages of CaCl₂, NaCl, and CaWO₄ were calculated to be 3.2, 3.3 and 1.1 V, respectively. In consideration of the inevitable *iR* drop and other kinetic barriers, the electrolysis voltages were controlled in the range between 2.2 and 3.1 V. In the voltage-dependent electrolysis, the electrolysis duration and temperature remained the same, i.e. 10 h and 1023 K, respectively. Fig. 4b presents the XRD patterns of corresponding samples. As can be seen, with increasing electrolysis voltage from 2.2 V to 3.1 V, the residual CaWO₄ after electrolysis decreases remarkably, rendering the trend that the higher the electrolysis cell voltage, the faster the electro-reduction of the pellet cathode. A reasonably high electrolysis voltage is essential to overcome the *iR* drop caused by large resistance of fine particles and loose structure of product (Fig. 2) and to ensure a practically acceptable production rate. In this regard, the electrolysis voltage was fixed at 3.1 V for the following experiments.

Duration-dependent constant-voltage electrolysis.—To obtain the detailed information of the electro-reduction process of CaWO₄ pellets in molten salt and to optimize the current efficiency, the pellets were electrolyzed for different durations (from 0 to 24 h) at 3.1 V, 1023 K. The corresponding XRD patterns of samples obtained from the duration-dependent electrolysis are exhibited in Fig. 5. According to Fig. 5, the electro-reduction of CaWO₄ pellet was enhanced with prolonged reaction time. In detail, the enhancement of electro-reduction against electrolysis time is much more significant during the initial 10 h (see Fig. 5a–e), while only minor enhancement occurs when further increasing the electrolysis duration from 10 to 24 h (see Fig. 5e–g). In addition, pure W product cannot be obtained until the electrolysis time lasts for more than 24 h, resulting in quite low current and production efficiencies. Especially, the electro-reduction of residual CaWO₄ becomes sluggish after 10 h of electrolysis, which deteriorates the overall energy efficiency. In addition, the current efficiencies of electrolysis for 10 and 24 h were calculated to be 54.56 and 25.48%, respectively. Based on the three-phase interlines model,^{10,11}

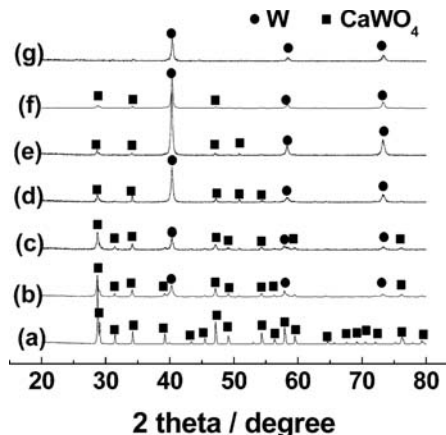


Figure 5. XRD patterns of samples obtained from electrolysis for (a) 0 h; (b) 2 h; (c) 5 h; (d) 8 h; (e) 10 h; (f) 20 h and (g) 24 h at 3.1 V, 1023 K.

the rate of electro-reduction of solid pellets in the depth direction (penetration) becomes progressively slower as a result of the rising ohmic and concentration polarizations. The electro-reduction of CaWO₄ pellet starts at the surface of the pellet at a fast rate,¹⁸ resulting in relatively high energy efficiency in the beginning of electrolysis. After then, the electro-reduction propagates into the inner parts of the pellet, where the longer oxygen diffusion path results in an increased concentration polarization, together with a high *iR* drop originating from the less-interconnected structure of generated fine particles. The increased ohmic and concentration polarizations across the inner part of pellets cause the barriers toward the complete electro-reduction of the residual CaWO₄ and then account for the low current efficiency in the later stage of electrolysis. This is also the reason why it needs 24 h to obtain pure W product.

Removing residual CaWO₄ by high temperature molten salt washing.—As mentioned in section 3.2, some unreduced CaWO₄ remained after electrolysis for 10 h at 3.1 V, 1023 K. The residual CaWO₄ can be fully reduced by prolonging electrolysis. However, the further electrolysis will inevitably lead to lower current efficiencies. Alternatively, a more energy-saving process was proposed and tested. After 10 h electrolysis of CaWO₄ pellet at 3.1 V, 1023 K, the electrolysis process was suspended and the temperature of molten salt was then elevated to 1123 K. The electrochemically reduced pellet was maintained in the same salt at this elevated temperature for 1 h. According to the CaWO₄ solubility test, solubility of solid CaWO₄ in the melt increases from 0.2 to 0.8 wt% with the increase of temperature from 1023 to 1073 K. At 1123 K, the residual CaWO₄ tends to dissolve into the melt quickly, leaving pure tungsten. The XRD patterns of the samples produced from 10 h electrolysis and the aforementioned washing process are exhibited in Fig. 6. As can

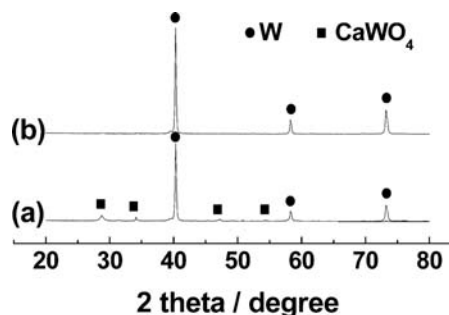


Figure 6. XRD patterns of the samples after the electrolysis for 10 h at 3.1 V, 1023 K without (a) or with (b) immersing the product in the same molten salt at 1123 K for 1 h.

Table I. Comparisons between two processes.

	Electrolysis for 24 h	Electrolysis for 10 h followed by washing for 1 h
Mass of CaWO ₄ pellet	1.9986 g	2.0005 g
Theoretical mass of product	1.2768 g	1.2781 g
Obtained mass of product	1.2448 g	1.2142 g
Yield	97.49%	95.00%
Theoretical charge	1087.8 mAh	1061.1 mAh
Practical charge	4268.6 mAh	1944.7 mAh
Current efficiency	25.48%	54.56%
Energy consumption	10.63 Wh (g W) ⁻¹	4.965 Wh (g W) ⁻¹

be seen, after the simple washing process in the same melt at higher temperature, residual CaWO₄ was removed, resulting in the formation of pure tungsten powder. On the other hand, the dissolution of CaWO₄ from precursor to the melt will inevitably decrease the productivity of tungsten. However, such a downgrade in yield is insignificant in our proposed washing process, since vast majority of precursory CaWO₄ has already been reduced during the first 10 h electrolysis.

As evidenced in Fig. 5, pure tungsten product could also be obtained after electrolysis for 24 h. Therefore, the two processes of electrolytic extraction of pure tungsten were compared in terms of yields, current efficiencies and electrolysis energy consumptions. As summarized in Table I, when compared with 24 h electrolysis, although a slight decrease in yield from 97.49 to 95.00% can be observed, the energy efficiency of the proposed extraction process significantly increases, with an improvement in current efficiency from 25.48 to 54.56% and a decrease in energy consumption from 10.63 to 4.965 Wh (g W)⁻¹. This analysis exhibits that, by using the washing process, the energy efficiency of tungsten extraction process is greatly enhanced without manifest compromise in yield.

Conclusions

In summary, the solubility of CaWO₄ in molten CaCl₂-NaCl eutectic at different temperature was measured. Based on the observation that the CaWO₄ solubility steeply increases at temperature higher than 1023 K, an unprecedented strategy on electrolytic extraction of fine tungsten powder was proposed and demonstrated by utilizing low-temperature and short-duration electrolysis of solid CaWO₄ followed by a simple washing process in the same melt but at a higher temperature. The proposed process shows a remarkable improvement in current efficiency and productivity and a vast decrease in energy consumption. Considering the reserves of tungsten resources, direct electrochemical production of pure tungsten from

scheelite (CaWO₄) is expected to have a potential application in industry.

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