

**Electrochemical Reduction of Tungsten Oxide in Molten LiCl-KCl Using a Novel Fluidised Bed Electrode Approach**

R. Abdulaziz<sup>1</sup>, L. D. Brown<sup>1</sup>, D. Inman<sup>1</sup>, S. Simons<sup>1,2</sup>, P. R. Shearing<sup>1</sup>, D. J. L. Brett<sup>1\*</sup>

<sup>1</sup>Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, United Kingdom  
<sup>2</sup>International Energy Policy Institute, UCL Australia, 220 Victoria Square, Adelaide, Australia  
 \*Email: d.brett@ucl.ac.uk

The direct electrochemical reduction of titanium oxide to titanium metal in molten CaCl<sub>2</sub> salt has been proven by the FFC Cambridge process. [1] Subsequently, the process has been applied to a number of refractory metals. However, there are limitations to the FFC Cambridge process. For example, the current efficiency of the process is quite low, 10-40%, to achieve sufficiently low oxygen content, 0.3%, in the final titanium product. [2] This could be due to a number of reasons, such as the increasing concentration of O<sup>2-</sup> ions in the melt as the reduction process proceeds. The metal oxide electrode has an inherent pore structure and sponge-type substrate electrodes can be used with a range of pore sizes, which has the advantage of high surface area and access of the melt to the oxide. However, when the metal oxide is reduced, oxide ions accumulation in the pores can significantly change the potential needed for the reduction, as shown in the Littlewood [3] predominance diagram (Figure 1). It can also result in the formation of other unwanted metal phases, such as those that include the salt's metal, as it reacts with the oxide ions. Oxide ion build up close to the electrode surface can ultimately bring the reduction process to a halt, leaving the inner parts of the metal oxide unreduced.

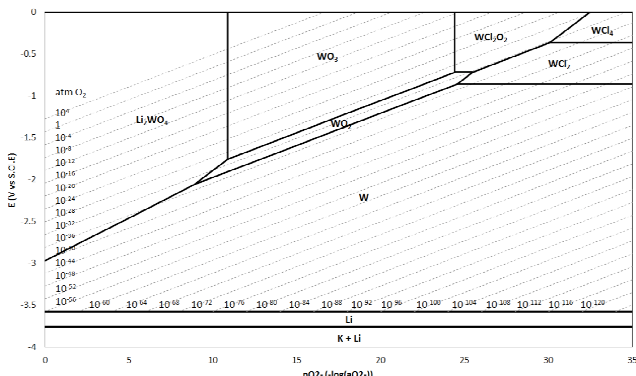


Fig.1: Predominance diagram for Li-K-W-O-Cl at 500°C

A possible solution to the O<sup>2-</sup> ions build-up issue is the utilization of a 'fluidised bed electrode' (FBE) which uses a suspension of metal oxide particles in an agitated electrolyte melt. A schematic of the arrangement used is shown in Figure 2. Fluidised bed electrodes have been studied and used industrially in various applications, [4] though their definition is not certain. They have not been applied in the FFC Cambridge molten salt processes. Here, tungsten is used as a model system; however the concept is applicable across a range of metal/oxides and molten salt systems. The cathode is a pure tungsten rod

and particles of tungsten oxide are in the LiCl-KCl eutectic melt. The oxide particles are agitated in the molten salt via the flow of argon bubbles from the bottom of the cell. The particles are reduced as they come into contact with the cathode rod. The reduced tungsten particles then either form on the surface of the cathode or precipitate at the bottom of the cell when the agitation is stopped. The anode is a graphite rod, separated from the melt and placed inside a glass tube fitted with a glass frit to avoid reoxidation of the tungsten. This approach is intended to eliminate the problems associated with the O<sup>2-</sup> ions and their formation on the surface of the cathode, and enable a more complete and efficient reduction of metal oxide to metal.

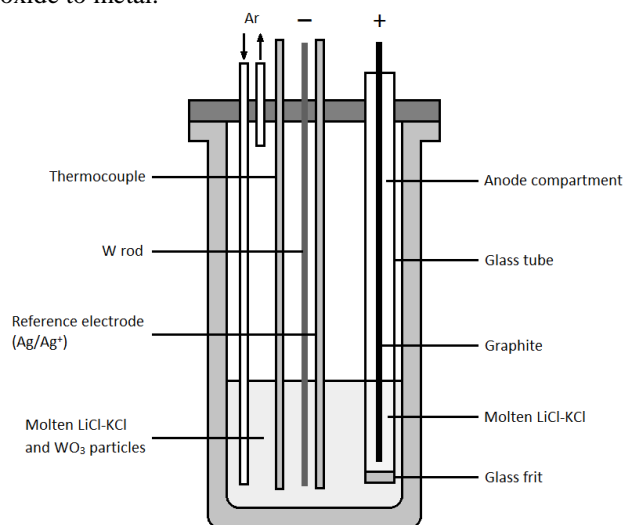


Fig.2: Schematic of the fluidised bed electrode cell

Figure 3 shows the voltammetry of a thin film of WO<sub>3</sub> compared to the fluidized bed electrode result if Figure 4, with a chronoamperometry over an extended period shown in Figure 5.

This paper discusses the experimental findings of the FBE applied to tungsten and its application to more technologically relevant systems such as the electrochemical reduction of uranium oxides to uranium, as being investigated in the EPSRC REFINE programme.

References:

1. Chen, G.Z., D.J. Fray, and T.W. Farthing, *Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride*. Nature, 2000. **407**(6802): p. 361-364.
2. Schwandt, C., D.T.L. Alexander, and D.J. Fray, *The electro-deoxidation of porous titanium dioxide precursors in molten calcium chloride under cathodic potential control*. Electrochimica Acta, 2009. **54**(14): p. 3819-3829.
3. Littlewood, R., *Diagrammatic Representation of the Thermodynamics of Metal-Fused Chloride Systems*. Journal of the Electrochemical Society, 1962. **109**(6): p. 525.
4. Coeuret, F., *The fluidized bed electrode for the continuous recovery of metals*. Journal of Applied Electrochemistry, 1980. **10**(6): p. 687-696.

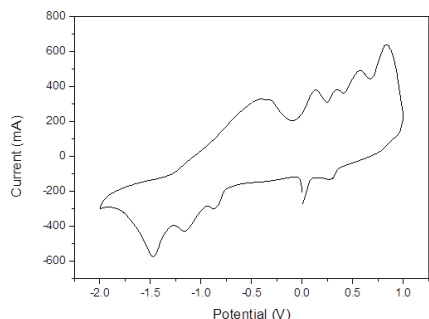


Fig.3: CV on WO<sub>3</sub> thin film

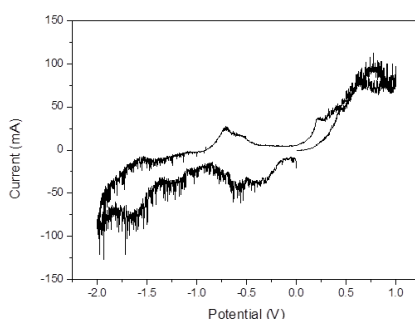


Fig.4: CV on WO<sub>3</sub> fluidised bed

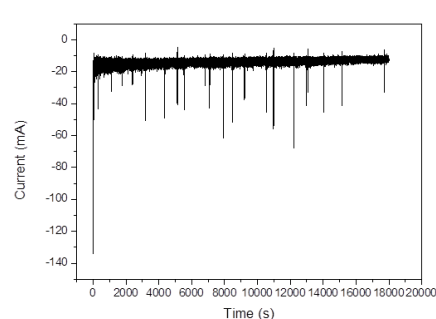


Fig.5: Chronoamperometry on WO<sub>3</sub> fluidised bed at -1.47V