Mechanism of soft solution processing formation of alkaline earth metal tungstates: an electrochemical and in situ AFM study

Abstract The mechanism of alkaline earth metal tungstate formation during soft solution processing was studied by cyclic voltammetry, electrochemical impedance spectroscopy and by direct in situ observation of the surface changes using atomic force microscopy. The electrochemical oxidation of W to WO$_3$ was followed by dissolution of WO$_3$ and, with some delay, by precipitation of tungstates at the metal surface. The same Tafel slopes observed in Li$^+$, Ba$^{2+}$, Sr$^{2+}$ and Ca$^{2+}$ containing solutions indicate that the course of the oxidation process is independent of the cation present in solution. The observed differences in the current-voltage curves outside the Tafel region are accounted for by the different film-forming tendencies of the various alkaline earth metal cations. The growth of tungstate layers at the W substrate decreases the electrochemically active area and limits the production of WO$_3^-$ at later stages of deposition. At low potentials ($E < 0.2$ V) the oxidation of W is the rate-controlling step. At higher potentials, however, the dissolution process slows down due to a relative decrease of the pH in the electrode vicinity and dissolution becomes the rate-limiting step.

Keywords Atomic force microscopy · Tungstates · Thin film deposition

Introduction

Soft solution processing (SSP) is one of the recent trends in the synthesis of advanced inorganic materials with controlled properties [1, 2]. By the term SSP we understand in this case the hydrothermal or electrochemical-hydrothermal treatment of starting materials to obtain the final product in a desirable shape. The preparation of double oxide thin films at a metal substrate is an example of the convenience of this processing. This method was successfully used to prepare materials like, for example, SrTiO$_3$ [3, 4], BaTiO$_3$ [5], LiNiO$_2$ [6, 7] and other materials, at temperatures below 200 °C. From the mechanistic point of view these processes can be described as oxidation of a transition metal followed by dissolution of the transition metal oxide and finally by crystallization (precipitation) of the double oxide from solution. The latter two steps may be considered as chemical ones. Anodic oxidation of a transition metal is, however, a complex process, the description of which is difficult, particularly at elevated temperatures (i.e. under hydrothermal conditions). This is also the reason why direct experimental confirmation of the proposed mechanism for film formation is lacking for most of the systems so far and no attempts to quantify the film formation process have been made.

The immediate goal of this study was to use an appropriate model system which would allow us to verify the proposed mechanism and to characterize the electrochemical and chemical parts of the process in terms of rate-controlling steps.

To avoid problems with instrumentation, we sought a metal/double oxide system proceeding at low temperature. Also the kinetics of film formation in the model system should be sufficiently fast to obtain compatible experimental timescales for both the method and the deposition process. Among several systems meeting the above-mentioned criteria, we selected the alkaline earth metal tungstates for this study. These materials can be prepared at room temperature on the timescale of $10^2$–$10^3$ s [8, 9, 10], which allows us to employ various electrochemical as well as in situ non-electrochemical approaches to describe the film formation. In this paper we present the results of cyclic voltammetry and electrochemical impedance spectroscopy.
(EIS), together with in situ atomic force microscopy (AFM) at constant potential to characterize the tungstate formation.

**Experimental**

Electrochemical experiments were carried out in a one-compartment glass cell, using a PAR 273 potentiostat complemented in impedance measurements by an EGG 5210 lock-in amplifier. Tungsten foil (0.2 mm thick, Nilaco, 99%) was used as a working electrode. All potentials were measured and are quoted with respect to an Ag/AgCl reference electrode; the three-electrode arrangement was complemented by a platinum auxiliary electrode. EIS was measured in the frequency range 100 kHz to 5 mHz with an a.c. amplitude of 10 mV (peak to peak). The electrode was subjected to a potentiostatic oxidation at 0.0 V for 5-40 min followed by an open circuit equilibration for 20 min prior to impedance measurement. Measured impedance data were analyzed by non-linear least-square (NLLS) fitting using Z-Plot/Z-View software (Scribner Associates).

The in situ AFM observations of the working electrode surface changes were carried out using a Pico scanning probe microscopy (Molecular Imaging) working in contact AFM mode (Si$_3$N$_4$ cantilever; force constant 0.12 N/m). A Pico potentiostat (Molecular Imaging) was used for polarization of the working electrode during the AFM scanning. Owing to the geometric restrictions, the Ag/AgCl reference electrode was substituted with a silver wire pseudo-reference electrode (PRE) in electrochemical AFM experiments. The potential of the Ag PRE was then quoted with respect to Ag/AgCl and the potentials were recalculated to the Ag/AgCl scale. Measurements were carried out in a solution containing $10^{-2}$ mol/L M(OH)$_2$ (M = Ba, Sr or Ca) (all p.a. grade Kanto Chemicals) and $10^{-1}$ mol/L NaClO$_4$ (p.a. grade Wako Chemicals) as a supporting electrolyte. For experiments in a Li-containing solution, LiOH (p.a. grade Wako Chemicals) in the same concentration was used instead of the alkaline earth metal hydroxides. All solutions were prepared using double distilled water, which was purged with Ar for 1 h to remove dissolved CO$_2$ and oxygen. The electrolyte solutions were kept under Ar prior to use.

![Fig. 1](image)

**Results and discussion**

The anodic behavior of tungsten electrodes in alkaline media has been covered in several papers [11, 12, 13, 14]. The overall process is described by the following equation:

$$W(s) + 8\text{OH}^- (aq) \rightarrow \text{WO}_4^{2-} (aq) + 4\text{H}_2\text{O} + 6e^- \quad (1)$$

Detailed analysis expects the whole process to be composed of four electrochemical and one chemical steps [14]. The dissolution rate of tungsten is proportional to the pH [11, 12] and is independent of the concentration of \(\text{WO}_4^{2-}\) in solution [14]. Cyclic voltammograms taken on a W electrode in the presence of some alkaline and alkaline earth metal cations are shown in Fig. 1. The voltammetric curve measured in Li$^+$ containing solution (where no double oxide film is formed) exhibits three pronounced current maxima at –206, 120 and 520 mV. The presence of several current peaks shows the complexity of the whole anodic process. According to quartz crystal microbalance (QCM) data [16], the peaks do not represent definite steps of the whole six-electron transfer, but appear rather due to an oxide accumulation at the electrode surface which proceeds at positive potentials [11, 12, 13]. This is caused by slowing of the \(\text{WO}_3\) dissolution owing to the relative lack of OH$^-$ in the electrode vicinity. Since the oxidation state of tungsten in this surface layer can be lower than VI, one can assign the positive current maxima to the oxidation of the previously accumulated oxide to oxidation state VI.

Cyclic voltammograms taken in the presence of alkaline earth metal cations differ for Ca$^{2+}$, Ba$^{2+}$ or Sr$^{2+}$ containing solutions. While in the case of Ca$^{2+}$ the measured voltammogram shape shows a good agree-