SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Effect of MWO₄ (M = Ca, Sr, Ba) Dispersion on the Interfacial Processes in $(+/-)WO_3|MWO_4|WO_3(-/+)$ Cells and Transport Properties of Metacomposite Phases

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Abstract—We compare data on the reciprocal electrosurface transfer (EST) of WO₃ and MWO₄ components through WO₃|MWO₄ eutectic heterointerfaces using MWO₄ (M = Ca, Sr, Ba) samples prepared by standard ceramic technology (CER) and nitrate-organic technology (N/O); these samples considerably differ in both the grain size of precursor powders and the grain size of sintered ceramics. When an electric field is applied, the interpenetration of WO₃ and MWO₄ components occurs though WO₃|MWO₄ (M = Ca, Sr, Ba) heteroint-

erfaces. The general $^{(-)}WO_3 \leftrightarrow MWO_4^{(+)}$ intermigration pattern in the cells is not influenced by tungstate

preparation technology. However, interpenetration rates are far greater for $MWO_4^{N/O}$. The transport properties of $\{MWO_4 \cdot xWO_3\}$ two-phase eutectic metacomposites manufactured by both technologies were studied. Tungstate and composite manufacturing technologies have no radical influence on the electric properties (overall and partial conductivity, transference numbers) of the samples, only changing conductivity versus concentration relationships. Our data well fit the model of formation of a nonautonomous electrolytic interphase.

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Processes occurring at homo- and heterointerfaces considerably influence the reactivity, thermodynamic, and kinetic stability of single-phase and composite nanostructured objects. The least studied and the most mysterious are electric-field-stimulated processes [1-3]. Solid-phase electrosurface phenomena include solid-phase electrocapillarity, field-induced electrosurface transport of oxides, electroosmotic migration, and a flow potential [1-3]. Field-stimulated reactionless pulling-in of WO₃ to the inner surface of CaWO₄ ceramic bricks was first described in [4, 5]. A very important discovery was the two-way character of both spontaneous and field-stimulated processes [1, 6]; WO_3 is pulled to the inner surface of MWO_4 ceramics, and in turn, MWO₄ components propagate (but in far smaller amounts) across the surface of WO₃, irreversibly changing their color. Further, this process was found to be intrinsic to all $WO_3 | MWO_4$ (M = Ca, Sr, Ba) interfaces [7].

In earlier works [1, 4-7], experiments on spontaneous and electrosurface transport through the WO₃|MWO₄ interface were carried out in symmetrical cells

(-)
$$Pt |WO_3| MWO_4 |WO_3| Pt (+)$$

(M = Ca, Sr, Ba) (1)

using MWO₄ samples prepared by standard ceramic technology. The following qualitative trends were observed in those works:

(1) As the amount of charge passage Q (C) increased, the WO₃ weight transferred to MWO₄ ceramics increased, too (the MWO₄ brick gained in weight), and accordingly, the WO₃ cathodic brick lost in weight; WO₃ as an autonomous phase filled-in a portion of the inner surface of MWO₄ ceramics. The greenish color front of the MWO₄ brick (the boundary of WO₃ penetration across the inner surface of the MWO₄ brick) propagated toward the (+) electrode; as a result, part of the MWO₄ brick adjacent to WO₃⁽⁻⁾,

converted to an {MWO₄ · xWO₃} composite.

(2) The $WO_3^{(+)}$ anodic brick had its weight virtually

unchanged; after the experiment was over, the $WO_3^{(+)}$ section was always lightened uniformly, but recovered its natural color as soon as after 1-h annealing in air at 800°C.

(3) The $WO_3^{(-)}$ section changed its color to dark green. Coloring started in the near- MWO₄ region, and as the current passed, the darkening zone gradually propagated across $WO_3^{(-)}$ in the direction of the Pt⁽⁻⁾

electrode and colored the entire thickness of the $WO_3^{(-)}$ brick. Additional annealing in air for 5 h at 1000°C did not change the dark-green color of the $WO_3^{(-)}$ section.

The interpretation of the above-described phenomenon was based on the solid-phase electrocapillarity model [1, 4, 5]. But the key role in electrosurface transfer (EST) is played by the deep transformation of the WO₃|MWO₄ heterointerface, namely, by the formation of a nonautonomous MW-*s* interphase, which has electrolytic conductivity ($(t_{0^{2-}} \approx 1)$ and, importantly, bilateral surface activity (2) and mobility (3) [1, 6, 7]:

$$\alpha_{\rm MW-s} < \alpha_{\rm WO_3} < \alpha_{\rm MWO_4}, \tag{2}$$

$$D_{\rm MW-s \to WO_3} \approx D_{\rm MW-s \to MWO_4}$$
 (3)

Most complete data in support of MW-*s* formation and the bilateral transfer of its components were gained by ESCA, high-temperature powder X-ray diffraction, and X-ray fluorescence analysis [7, 8].

Perhaps, the most unexpected result was the fieldstimulated pulling-in of the MW-s electrolytic interphase to the inner surface of the electron-conducting WO₃ and its grain-boundary migration in the "–" direction. Noteworthy is the recent substantiation of a hypothesis that the irreversible darkening of the WO₃⁽⁻⁾ brick arises from the appearance of a dense film of an M–W tetragonal bronze phase on grain surfaces of the WO₃⁽⁻⁾ brick [9].

The above-described data were obtained in experiments on micron-sized MWO_4 ceramics prepared by ceramic technology. However, inasmuch as spontaneous and field-stimulated migrations of oxides are developed on the inner surfaces of ceramic bricks, it is reasonable to suggest that the process rates would depend on the degree of surface development, that is, on the MWO₄ grain size.

Here we gain data on the EST of WO_3 to MWO_4 ceramics with far smaller grain sizes prepared by nitrate-organic technology. EST rates, conductivities, and transference numbers are compared between MWO_4 ceramics and $\{MWO_4 \cdot xWO_3\}$ composites prepared by the aforementioned nitrate-organic and ceramic technologies.

EXPERIMENTAL

Synthesis. The ceramic procedure for manufacturing MWO₄ ceramics and $\{(1 - x)MWO_4 \cdot xWO_3\}$ (hereafter, $\{MWO_4 \cdot xWO_3\}$) composites is descried in [4, 5]. The precursors for nitrate-organic technology were ammonium paratungstate $(NH_4)_{10}W_{12}O_{41}$ (pure for analysis grade), MCO₃ (high purity grade 16-2), (M = Ca, Sr, Ba), tartaric acid C₄H₆O₆ (pure for analysis grade), and aqueous (1 : 3) nitric acid HNO₃ (high purity grade 8-4). The MCO₃ precursor samples were calcined at 400–600°C before use. Tungsten oxide WO₃ in $(NH_4)_{10}W_{12}O_{41}$ was determined gravimetrically by calcining to constant weight at 500°C. The WO₃ percentage was 88.78 wt %.

The nitrate-organic synthesis of MWO_4 and its composites is illustrated by the scheme below.



We calculated weights of alkaline-earth carbonates and ammonium paratungstate $(NH_4)_{10}W_{12}O_{41}$ required to prepare MWO₄ and {MWO₄ · *x*WO₃} (*x* = 0–0.3) composites.

To prepare solution (*a*) MCO_3 was placed in a vessel containing 25 mL water followed by slow addition of then dilute HNO_3 . Vigorous carbon dioxide gas evolution was observed.

 $(NH_4)_{10}W_{12}O_{41}$, together with a twofold weight excess of tartaric acid $C_4H_6O_6$, was dissolved in 125 mL water under moderate heating. Yellowish solution (b) was obtained. Solution (a) was slowly poured to warm (40–50°C) solution (b) under stirring. The resulting solution was working solution (c), which contained all necessary components. Solution (c) was transferred to a ceramic cup and concentrated to dryness to obtain a yellow waxy intermediate product, which then rapidly crystallized at room temperature. The intermediate product was calcined with temperature elevated in steps from 700 to 900°C and intermittent grinding in an agate mortar.

The MWO₄^{N/O} (M = Ca, Sr, Ba) powders were synthesized with grain sizes of 80–100 nm (Shimadzu SALD 7101 grain size analyzer). MWO₄^{CER} (M = Ca, Sr, Ba) powders had grain sizes of 3–7 μ m (SEM). Reactive WO₃ grains had sizes of 2–5 μ m (SEM).

MWO₄ and composite blends were compacted on a hand-operated hydraulic press in a steel mold ($p_{comp} = 640 \text{ kg/cm}^2$). Bricks (2–5 × 10) were sintered for 6 h at 930°C and then polished to obtain plane-parallel sur-



Fig. 1. WO₃ weight transferred to MWO₄ ceramics vs. electricity amount; $T = 900^{\circ}$ C, I = const = 1 mA.



Fig. 2. Transference number vs. temperature for $\{SrWO_4 \cdot xWO_3\}$ and $\{BaWO_4 \cdot xWO_3\}$ composites (prepared by N/O technology.

faces. The relative densities of the samples were 0.75-0.80.

Electron microscopic investigations were carried out using Hitachi S-4100 and JCXA-733 electron microscopes.

Particle sizes of MWO₄^{N/O} sintered ceramics were $1.0-1.5 \ \mu\text{m}$; those of MWO₄^{CER} sintered ceramics were $\approx 5-10 \ \mu\text{m}$.

Experimental field-stimulated migration data were obtained with the use of electrochemical cell (1) at 900°C. Platinum electrodes were shaped as platelets. The assembly was placed into a furnace preheated to the required temperature. The isothermal exposure temperature was reached within 10 min. Then, the potential was applied to the system from a B5-49 source. The current was maintained at $I \approx 1$ mA. Various amounts of electricity were passed through the cells.

The course of the process was monitored by weighing the contacting bricks before and after annealing on a Sartorius analytical balance with an error of 0.0001 g. Transference numbers $t_{0^{2-}}$ were determined by the emf method in the cell

$$a'_{O_{2=0,21}}$$
 (Pt)|{MWO₄ · xWO₃}|(Pt) $a''_{O_{2=1}}$ (4)

The details of the procedure are found in [10].

Conductivity measurements were carried out on an IPU-1 virtual impedometer in the frequency range $50-10^5$ Hz. Some measurements were performed at 1 kHz.

RESULTS AND DISCUSSION

Electrosurface Transfer

This work mostly concerns $M^{2+} = Sr$ or Ba, because previous works [1, 4, 6, 7, 10] mainly concerned electrosurface transfer in CaWO₄. The electrosurface transfer experiments here were carried out in a galvanostatic mode, where the current had a fixed value of 1 mA. Charges of up to 90 C were passed through the cells. The process rate was judged from the gain in MWO₄ brick weight per unit time for a fixed current: $V_{\text{EST}} = (\Delta m/\tau)_{I=1\text{mA}}$.



Fig. 3. Transference number vs. concentration for $\{SrWO_4 \cdot xWO_3\}$ and $\{BaWO_4 \cdot xWO_3\}$ composites prepared by various methods.

The curves plotted in Fig. 1 present the tungsten oxide weight transferred to MWO_4 ceramics. These curves definitely show that the electrosurface migration of tungsten oxide to the ceramics prepared by nitrate-organic technology occurs at far higher rates than in ceramic samples:

$$V_{\text{EST}}(\text{WO}_3 \longrightarrow \text{CaWO}_4^{\text{N/O}}) / V_{\text{EST}}(\text{WO}_3)$$

$$\longrightarrow \text{CaWO}_4^{\text{CER}}) \approx 2.0$$
(5)

and

$$V_{\text{EST}}(\text{WO}_3 \longrightarrow \text{SrWO}_4^{\text{N/O}}) / V_{\text{EST}}(\text{WO}_3)$$

 $\longrightarrow \text{SrWO}_4^{\text{CER}} \approx 2.7.$ (6)

The different EST rates most likely arise both from the smaller grain size of N/O ceramics (i.e., the greater inner surface accessible to accommodate WO₃) and from the specifics of N/O technology, where grain surfaces are washed from the WO₃-containing impurity phase (see scheme). Finally, the purer and fresher surfaces of $MWO_4^{N/O}$ ceramics are more susceptible (more adhesion-active) to coverage with a WO₃ flow. However, it is well known that MWO_4^{CER} ceramics, even though being nominally stoichiometric, are always coated ("poisoned") by a film of an MW-s nonautonomous phase, whatever it has a minimal thickness [1, 2–8], which evidently reduces the WO₃ pulling-in rate.

The foregoing is verified by the EST current efficiency ratio (χ), a value showing the number of WO₃ g-equivalents transported by the 1 F charge [4, 5],

$$\chi = \frac{\Delta m_{\rm WO_3}}{M_{\rm WO_3}} "z_{\rm WO_3}" \frac{F}{Q},$$
(7)

where Δm_{WO_3} is the transported WO₃ weight, M_{WO_3} is the molar weight of a WO₃ mole, " z_{WO_3} " is the number of WO₃ g-equivalents per mole (z = 6), and Q is the charge passed through the system (coulombs).

$$\chi^{N/O}_{CaWO_4} = 0.97; \quad \chi^{CER}_{CaWO_4} = 0.45 \\ \chi^{N/O}_{SrWO_4} = 0.99; \quad \chi^{CER}_{SrWO_4} = 0.41$$
(8)

For MWO₄^{N/O}, $\chi_{MWO_4}^{N/O}$ values are close to the limiting value $\chi = 1$.

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Fig. 4. Ion conductivity vs. concentration for $\{SrWO_4 \cdot xWO_3\}$ and $\{BaWO_4 \cdot xWO_3\}$ composites prepared by various methods.

Transference Numbers and Conductivity

Figure 2 shows ion transference numbers as a function of temperature in $\{MWO_4 \cdot xWO_3\}$ (M = Sr, Ba) composites. We refer the experimentally determined transference numbers to the oxygen conductivity contribution because earlier works [11, 12] substantiated that oxygen is the majority ion charge carrier in scheelite-related compounds and materials.

Analyzing the data obtained for the {MWO₄·xWO₃} (M = Sr, Ba) composites (Fig. 2), we infer the following:

(i) For most (N/O) composites having $0 < t_{0^{2-}} < 1$ (mixed conductors), $t_{0^{2-}}$ either increases with rising temperature or remains unchanged, whereas for $\{MWO_4^{(CER)} \cdot xWO_3\}$ (M = Sr, Ba), the respective value always drops in response to rising temperature. This trend might signify the different transport properties of $MWO_4|WO_3$ interfaces in composites prepared by different technologies. Recall that a similar behavior of $t_{0^{2-}}(T)$ has been earlier described and analyzed for $\{CaWO_4^{(CER)} \cdot xWO_3\}$ composites [5], which were also manufactured by ceramic synthesis.

(ii) The electrolytic region for the composites prepared by nitrate-organic technology was $x \le 0.15$, whereas for ceramically synthesized samples it was slightly greater and reached x = 0.20 (Fig. 3).

The {MWO₄^{N/O} · *x*WO₃} (M = Sr, Ba) composites synthesized and characterized in this work, as well as previously studied {CaWO₄^(CER) · *x*WO₃}, are classified as metacomposites [10], because the properties of a composite as a whole are not intrinsic to any of its constituent.

Resuming, we find that the preparation technology and grain size are most decisive for the electrosurface transfer rate, while the transport properties of multiphase $MeWO_4$ and their composites are far less sensitive to the preparation technology and grain size.

Pertinently, the aforementioned trends are related to the fact that, during EST in cells with $MWO_4^{N/O}$, the incorporation of WO_3 and its propagation occur at MWO_4 grain surfaces, which are nominally "pure" (see above) and free of impurity phases.

On the contrary, the $WO_3|MWO_4$ interface appears coated with a surface-active and kinetically active phase WO_3 -s as early as at the sintering stage. This induces recrystallization of $MWO_4^{(N/O)}$ matrix grains



Fig. 5. SEM images and EDA analysis of cleaves from contact surfaces of $WO_3^{(-)}$ and $CaWO_4^{N/O(+)}$ bricks after annealing in cell (1).

and changes the transport properties of the inner surface of N/O ceramics. As a result, the conductivities and transference numbers of N/O and CER samples converge.

However, there are substantial distinctions, in particular, in the initial segments of the $\sigma_{ion}(x)$ plots where $0 < x \le 0.2$ (Fig. 4). For N/O samples, we observe a nearly monotonic rise in σ_{ion} , while for CER samples characteristic is a local plateau starting at small *x*. This behavior is explained by different grain sizes and S_{sp} of composites manufactured by different technologies. MWO₄^{CER} samples have large grains and relatively small inner surface areas. In this case, a small WO₃ amount is sufficient for forming a through film of an ion-conductive WO₃-*s* interphase with the thickness providing a maximal total ionic conductivity (the plot enters a local plateau). For MWO₄^{N/O} samples (having smaller grain sizes and greater inner surfaces), increasing *x* leads to a systematic increase in connectivity and in film thickness of the WO₃-s phase, which is manifested as the monotonic rise in σ_{ion} .

Further, the aforementioned increase in $t_{O^{2-}}$ in response to temperature elevation for most (N/O) composites having $0 < t_{O^{2-}} < 1$ (mixed conductors), indicates a considerable dependence of the ion transport parameters on the technology and morphology of the ceramics. The nature of this dependence is to be understood, which will be done elsewhere.

Recall that the key role in EST is played by the MW-*s* nonautonomous interphase, which exists only within a limited range of high temperatures [1, 5, 13]. Another piece of evidence in favor of the existence of this phase is provided by the SEM inspection of the products of its decomposition in interface regions carried out after the contact annealing of the CaWO₄^{CER} |WO₃ couple [7, 13].

Here, we carried out similar SEM–EDA studies but for near-contact regions of the $(+)CaWO_4^{N/O}|WO_3(-)$ couple. The exfoliation and peeling of a WO₃-based film (as probed by EDA) is well seen in the SEM image of the surface of a CaWO₄^{N/O} brick across which the WO₃ phase propagated from the WO₃⁽⁻⁾ electrode (Fig. 5). In turn, calcium-containing precipitates of tubular shapes are observed on a chip of a WO₃⁽⁻⁾ brick after contact with CaWO₄ (as probed by EDA). Both film and tubular precipitates are the degradation products of the MW-*s* nonautonomous phase, which is stable only within a limited range of high temperatures (see above). The aforementioned pattern is a complete analogue of what was observed for the CaWO₄^{CER} |WO₃ couple [7, 13]. This shows that the nature of interfacial processes is not affected by the preparation technology and morphology of MWO₄ ceramics.

To summarize, in (-) $Pt|WO_3|MWO_4|WO_3|Pt$ (+) (M = Ca, Sr, Ba) cells we studied reciprocal electrosurface transfer of WO₃ and MWO₄ components through WO₃|MWO₄ eutectic heterointerfaces. MWO₄ ceramics were manufactured using ceramic technology (CER) and nitrate-organic technology (N/O). $MWO_4^{N/O}$ grain sizes are one order of magnitude smaller than MWO_4^{CER} grain sizes. Qualitatively, ${}^{(-)}\!W\!O_3 \longleftrightarrow MeWO_4^{(+)}$ intermigration has a similar pattern. For $MWO_4^{N/O}$ however, the electrosurface transfer rates are two to three times as high. We have shown that technology used to manufacture tungstates and $\{MWO_4 \cdot xWO_3\}$ two-phase metacomposites only insignificantly influences the ion conductivity versus concentration dependences and the electrolytic range. The trends we discovered go in line with the model of the formation of an electrolytic nonautonomous interphase and its key role in the genesis of electrosurface transfer. SEM-EDA supplied us with evidence for the formation and intermigration of a nonautonomous MW-s phase in the vicinity of the $MWO_4^{N/O}|WO_3$ interface.

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