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## Catalytic Mo<sub>2</sub>C Coatings for the Water Gas Shift Reaction: Electrosynthesis in Molten Salts

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**Abstract**—Electrosynthesis methods using molten salts are suggested for obtaining a new catalytic system based on the Mo<sub>2</sub>C/Mo composition for the water gas shift reaction. The coatings obtained by the discharge of the carbonate ion on a molybdenum substrate and by the simultaneous reduction of the electroactive species MoO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> are catalytically more active than bulk Mo<sub>2</sub>C or the commercial catalyst Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> by one and three orders of magnitude, respectively.

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A promising area of hydrogen energy engineering is design of integrated on-board power supply units consisting of a fuel processor and a fuel cell. The conversion of a fuel, e.g., natural gas, in the processor yields hydrogen containing 8–12 vol % CO. The CO concentration is then reduced to 0.1 vol % in the fuel processor via the water gas shift (WGS) reaction. This is necessary because CO is poisonous to the proton exchange reaction of the fuel cell.

A catalyst intended for the WGS reaction in an automotive fuel processor should be sufficiently active in the required temperature range, stable over at least 5000 h, and not pyrophorous (unlike the industrially used catalyst Cu–ZnO–Al<sub>2</sub>O<sub>3</sub>) and should not require any lengthy prereduction procedure. The Mo<sub>2</sub>C catalyst is more active [1–6] and more stable under the WGS conditions [7–9] than the Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst. There have been several studies devoted to the effects of nickel and cobalt incorporated in the carbide layer [10, 11]. However, the activity of these modified catalysts decreases during the reaction because of the agglomeration of the incorporated particles.

The main method used in the synthesis of molybdenum carbide on a molybdenum substrate is the oxidation of a molybdenum plate in flowing dry air (50 ml/min) at 673 K for 16 h. In the presence of oxygen, molybdenum oxidizes above 623 K into orthorhombic MoO<sub>3</sub>, the oxide that is thermodynamically most stable under these conditions [12]. It can be reduced to hexagonal Mo<sub>2</sub>C (containing <10 wt % cubic Mo<sub>2</sub>C) in a flowing hydrogen + methane (20 vol %) mixture under continuous heating from 300 to 973 K with a 30-min-long stay at the highest temperature point [3].

Molybdenum carbide electrosynthesis from molten salts offers some advantages over the other methods.

For example, electrochemical methods using a pulse or reversing current make it possible to easily control the structure of the resulting deposit; the thickness, porosity, roughness, and texture of the electrodeposited coating; and the grain size of the resulting phase (down to the nanometer level). The other advantages are as follows: (1) the synthesis temperature is comparatively low (973–1123 K); (2) the electrodeposition parameters determined in the laboratory are valid for large-scale apparatuses and can be adjusted to complex-shaped substrates in such a way that the thickness, grain size, and composition of the coating remain uniform; (3) the resulting coatings are very pure even if the starting chemicals are of poor quality; (4) the purchase price and maintenance costs of the electrochemical equipment are comparatively low.

### EXPERIMENTAL

#### Mo<sub>2</sub>C Synthesis

Molybdenum carbide coatings on a molybdenum substrate were electrosynthesized by galvanostatic electrolysis using the salt systems NaCl–KCl–Li<sub>2</sub>CO<sub>3</sub> (1), NaCl–KCl–Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>MoO<sub>4</sub> (2), and LiCl–KCl–Li<sub>2</sub>C<sub>2</sub> (3).

The alkali metal chlorides (Prolabo, 99.5 wt %) were pretreated by prolonged gradual heating to temperatures above their melting points in an HCl atmosphere in quartz tubes. Excess HCl was removed from the melt by purging it with argon. Until use, the salts were stored in sealed glass tubes in a glovebox. Li<sub>2</sub>CO<sub>3</sub> (reagent grade) and Na<sub>2</sub>MoO<sub>4</sub> · 2H<sub>2</sub>O (reagent grade) were dried for 24 h at 473 K. Li<sub>2</sub>C<sub>2</sub> was synthesized in situ from the molten LiCl–KCl eutectic by discharging

Li<sup>+</sup> cations on a graphite cathode at a cathodic current density of 2 A/cm<sup>2</sup>.

Alkali metal chlorides were combined in appropriate proportions and were charged into a glassy carbon tube (SU-2000). The tube was then placed into a stainless steel retort. The retort was pumped to a residual pressure of 0.67 Pa first at room temperature and then at 473, 673, and 873 K. The cell was heated in a programmed mode using a furnace equipped with a Termomatik-L temperature controller. Temperature was measured with a Pt/Pt-Rh (10 wt % Rh) thermocouple. The retort was filled with high-purity argon (<3 ppm H<sub>2</sub>O, <2 ppm O<sub>2</sub>), and the electrolyte was melted. Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>MoO<sub>4</sub> were added to the alkali metal chloride melt.

The molybdenum plates (99.99 wt % Mo) were 40 mm in length, 10 mm in width, and 0.1 mm in thickness. In order to remove the organic impurities from the surface, the molybdenum plates were placed in boiling xylene for 1 h and were then heated in a furnace at 413 K to desorb the xylene that remained on the surface. The molybdenum plates were immersed into the melt through a hole in the upper part of the retort. Mo<sub>2</sub>C on molybdenum plates was synthesized at 1123 K for 7 h at a cathodic current density of 5 mA/cm<sup>2</sup> for systems 1 and 2 and an anodic current density of 5 mA/cm<sup>2</sup> for system 3. In systems 1 and 2, the anode was the glassy carbon (SU-2000) tube. The samples resulting from the experiment were washed with distilled water and ethanol and weighed.

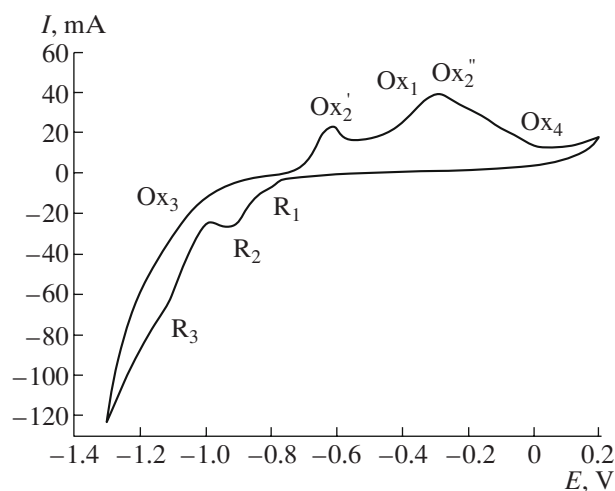
The BET surface area of the Mo<sub>2</sub>C samples obtained from melts 1–3 was 18, 38 (tentative value), and 11 m<sup>2</sup>/g, respectively. The apparent density of the carbide was 4.0 g/cm<sup>3</sup>. The specific surface area of the commercial catalyst and bulk Mo<sub>2</sub>C is 60 and 61 m<sup>2</sup>/g [1], respectively.

### Electrochemical Cell

Electrochemical studies were carried by cyclic voltammetry with linear potential scan on a VoltaLab-40 potentiostat using the VoltaMaster 4 software (version 6). The potential scan rate ( $\nu$ ) was varied between  $5 \times 10^{-3}$  and 2.0 V/s. The experiments were made in the temperature range 973–1123 K. Cyclic voltammograms were recorded using a molybdenum or glassy carbon (GC) working electrode 0.5–2 mm in diameter. The potential was measured versus a platinum wire, which served as the quasi-reference electrode Pt-PtO<sub>x</sub>-O<sup>2-</sup> [13], or versus the reference electrode Ag/NaCl-KCl-AgCl (2 wt %). The GC crucible served as the auxiliary electrode.

### Catalytic Activity Measurements

Prior to the determination of their catalytic activities, the coatings were treated with flowing hydrogen for 12 h while being gradually heated to 753 K at a rate



**Fig. 1.** Cyclic voltammogram of the molybdenum electrode in the NaCl-KCl-Li<sub>2</sub>CO<sub>3</sub> melt. The electrode surface area is 0.238 cm<sup>2</sup>, the polarization rate is 0.1 V/s,  $T = 1023$  K, and  $C_{\text{Li}_2\text{CO}_3} = 2.37 \times 10^{-4}$  mol/cm<sup>3</sup>.

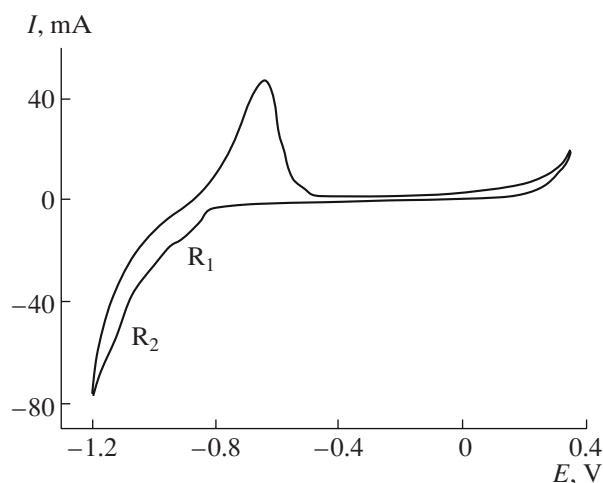
of 1 K/min. Ten Mo<sub>2</sub>C/Mo plates were mounted parallel to one another in a microstructured flow reactor, spaced at 500- $\mu$ m intervals. The reactor was heated with a Carbolite resistance furnace. The gas mixtures entering and leaving the reactor were analyzed online using a Varian GC (CP-3800) gas chromatograph with poraPLOT-U and molecular sieve 5 Å columns (0.25 mm  $\times$  10 m) and a thermal-conductivity detector. The CO conversion measured at atmospheric pressure and  $T = 463$ – $633$  K did not exceed 15%. This allowed us to use the differential reactor model in the calculation of kinetic parameters. The reaction was conducted under the following conditions:  $P_{\text{CO}} = 300$  Pa,  $P_{\text{H}_2\text{O}} = 760$  Pa,  $P_{\text{CO}_2} = 1.2$  kPa,  $P_{\text{H}_2} = 40$  kPa, He as the balance, and  $V = 50$  cm<sup>3</sup>/min.

## RESULTS AND DISCUSSION

### Electrode Processes Accompanied by the Electroreduction of Molybdenum Carbides

The voltammogram recorded for the NaCl-KCl-Li<sub>2</sub>CO<sub>3</sub> melt with a molybdenum electrode at a polarization rate of 0.1 V/s is presented in Fig. 1. The voltammogram shows three cathodic waves (R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>) and the corresponding electrooxidation peaks (Ox<sub>1</sub>, Ox<sub>2</sub>, Ox<sub>3</sub>). Since the electrode processes in the chloride-carbonate melt were discussed in detail in our earlier publication [14], here we will briefly consider only the electrode reactions that are involved in the molybdenum carbide synthesis.

We found that the height of the wave R<sub>1</sub> decreases with an increasing polarization rate and is not observed

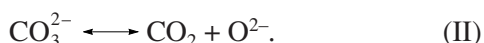


**Fig. 2.** Cyclic voltammogram of the molybdenum electrode in the NaCl-KCl-Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>MoO<sub>4</sub> melt. The electrode surface area is 0.238 cm<sup>2</sup>, the polarization rate is 0.1 V/s,  $T = 1023$  K,  $C_{\text{Li}_2\text{CO}_3} = 4.61 \times 10^{-5}$  mol/cm<sup>3</sup>, and  $C_{\text{Na}_2\text{Mo}_4} = 9.63 \times 10^{-5}$  mol/cm<sup>3</sup>.

in the voltammograms recorded at  $v \geq 1.0$  V/s. Potentiostatic electrolysis at potentials corresponding to the wave R<sub>1</sub> results in the formation of Mo<sub>2</sub>C on the molybdenum electrode. The cathodic current density in the region of wave R<sub>1</sub> potentials is low because of the low concentration of carbon-containing electroactive species. The wave R<sub>1</sub> is due to the discharge of CO<sub>2</sub>, whose solubility in the NaCl-KCl melt is  $(6-8) \times 10^{-8}$  mol/cm<sup>3</sup> [15]. This electrode process can be represented as

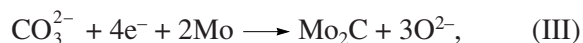


In the presence of the carbonate ion, reaction (I) is preceded by the chemical reaction

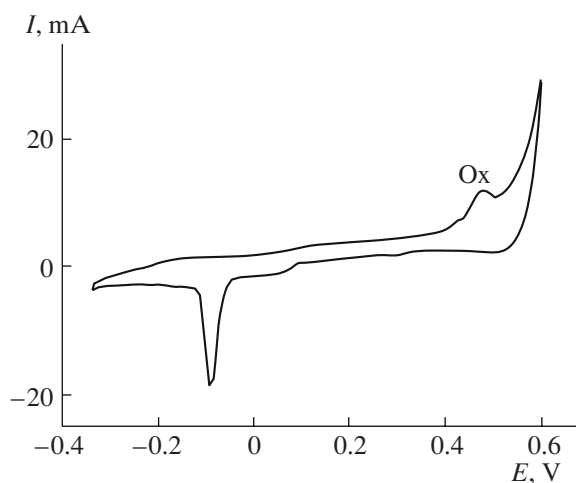


Raising the polarization rate causes a decrease in the CO<sub>2</sub> concentration in the melt and, accordingly, reduces the wave R<sub>1</sub>.

Single-phase Mo<sub>2</sub>C results from potentiostatic electrolysis at a potential of -0.850 V versus the platinum quasi-reference electrode, that is, at the base of the wave R<sub>2</sub>. The phase MoC results from potentiostatic electrolysis at -0.887 V and more negative potentials, which correspond to the wave R<sub>2</sub>. Thus, the electrode processes giving rise to the wave R<sub>2</sub> can be represented as

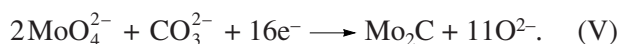


In the cathodic half-cycle, process (III) and (IV) are not resolved in the voltammograms because of the similarity of their discharge potentials.

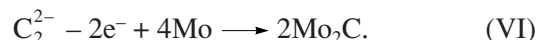


**Fig. 3.** Cyclic voltammogram of the molybdenum electrode in the LiCl-KCl-Li<sub>2</sub>C<sub>2</sub> melt. The electrode surface area is 0.238 cm<sup>2</sup>, the polarization rate is 0.1 V/s,  $T = 1123$  K, and  $C_{\text{Li}_2\text{C}_2} = 3.12 \times 10^{-5}$  mol/cm<sup>3</sup>.

The voltammogram of the molybdenum electrode in the NaCl-KCl-Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>MoO<sub>4</sub> melt is shown in Fig. 2. The cathodic half-cycle of this voltammogram has at least two well-defined waves, namely, R<sub>1</sub> and R<sub>2</sub>. Potentiostatic electrolysis at the wave R<sub>1</sub> potential yields Mo<sub>2</sub>C, and the same process at the wave R<sub>2</sub> potential yields a two-phase cathodic product consisting of Mo<sub>2</sub>C and MoC. In general form, simultaneous CO<sub>3</sub><sup>2-</sup> and MoO<sub>4</sub><sup>2-</sup> electroreduction yielding Mo<sub>2</sub>C can be represented as the following reaction:



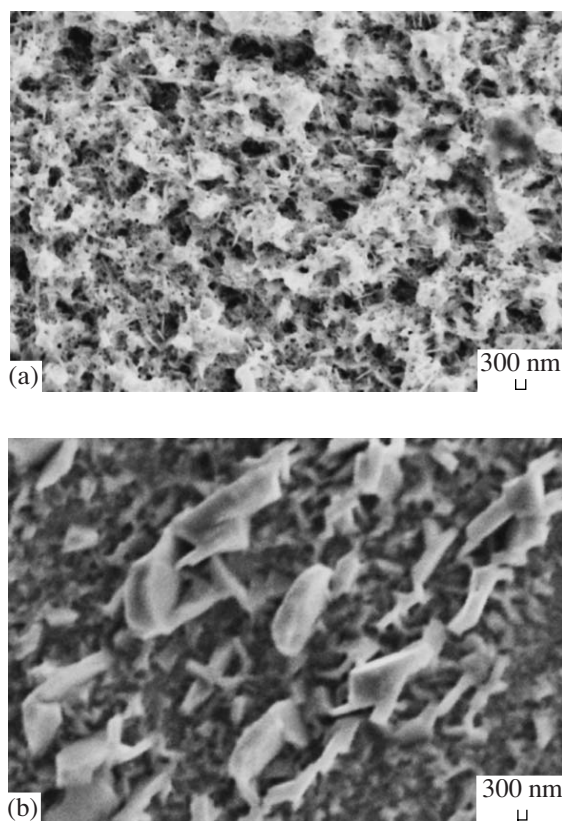
Lithium carbide dissociation in the LiCl-KCl-Li<sub>2</sub>C<sub>2</sub> melt yields the electroactive species C<sub>2</sub><sup>2-</sup>, so the synthesis of Mo<sub>2</sub>C is possible on an anodically polarized molybdenum substrate (Fig. 3, wave Ox in the voltammogram). This synthesis is described by the electrooxidation reaction



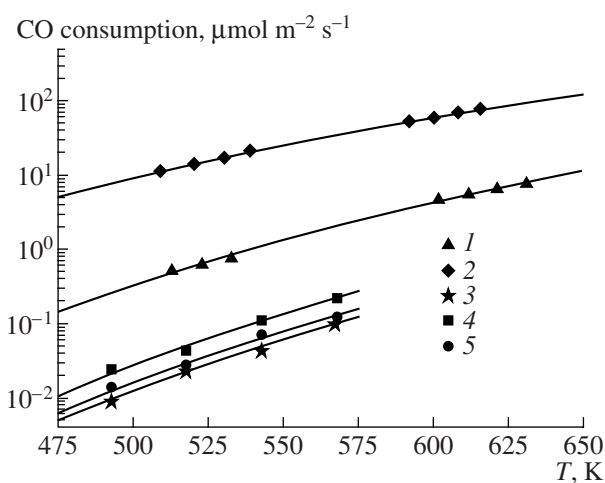
#### Characteristics and Catalytic Activity of the Mo<sub>2</sub>C/Mo Coatings

Electrosynthesis in melts 1-3 always yields hexagonal molybdenum semicarbide, while bulk Mo<sub>2</sub>C usually has a cubic lattice. The formation of hexagonal Mo<sub>2</sub>C in the electrosynthesis is due electrocrystallization taking place under specific conditions (electric field, double layer, and high temperature).

The diffraction patterns from the Mo<sub>2</sub>C coatings synthesized on molybdenum substrates in systems 1



**Fig. 4.** Morphology of the molybdenum carbide coatings synthesized on molybdenum substrates from the (a) NaCl–KCl–Li<sub>2</sub>CO<sub>3</sub> (5.0 wt %) and (b) NaCl–KCl–Li<sub>2</sub>CO<sub>3</sub> (1.5 wt %)-Na<sub>2</sub>MoO<sub>4</sub> (8.0 wt %) melts at  $T = 1123$  K and a current density of 5 mA/cm<sup>2</sup>. The coating thickness is (a) 0.5 and (b) 53.8  $\mu$ m.



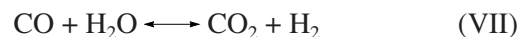
**Fig. 5.** Temperature dependence of the WGS reaction rate on the catalysts (1) Mo<sub>2</sub>C (system 1), (2) Mo<sub>2</sub>C (system 2), (3) Mo<sub>2</sub>C (system 3), (4) bulk Mo<sub>2</sub>C, and (5) Cu–ZnO–Al<sub>2</sub>O<sub>3</sub>.

and 3 contain reflections from molybdenum metal. For system 2, these reflections are missing. Therefore, the thickness of the coatings obtained from melts 1 and 3 differs from the thickness of the Mo<sub>2</sub>C coating synthesized in system 3.

The thickness of the Mo<sub>2</sub>C coatings obtained in systems 1 and 3 is as small as 0.5–2.0 and 0.3–0.5  $\mu$ m, respectively, because molybdenum carbide, like other refractory-metal carbides, forms excellent barrier layers and, as a consequence, the molybdenum–carbon interdiffusion coefficient is reduced by several orders of magnitude. The simultaneous electroreduction of MoO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> (system 2) yields Mo<sub>2</sub>C coatings ~50  $\mu$ m in thickness.

Figure 4 shows the morphology of the Mo<sub>2</sub>C coatings obtained from the NaCl–KCl–Li<sub>2</sub>CO<sub>3</sub> and NaCl–KCl–Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>MoO<sub>4</sub> melts at 1123 K, a cathodic current density of 5 mA/cm<sup>2</sup>, and an electrolysis time of 7 h.

The steady-state rate of the WGS reaction,



for the Mo<sub>2</sub>C/Mo composition obtained from melt 3 is somewhat lower than the rate of the same reaction over the commercial catalyst (Fig. 5) because of the small thickness and small specific surface area of the coating.

The steady-state reaction rate per unit surface area for the Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> samples synthesized in melts 1 and 2 is higher than the same characteristic of bulk Mo<sub>2</sub>C or the commercial catalyst Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> by one and three orders of magnitude, respectively (Fig. 5). Taking into account the apparent density and specific surface area data for Mo<sub>2</sub>C synthesized by different methods, it is possible to characterize the activity of molybdenum carbide in terms of reaction rate per unit weight of the catalyst. No methane formation is observed throughout the temperature range in which the Mo<sub>2</sub>C/Mo coatings were examined. The catalytic activity of the coatings remains constant over an on-stream time of 500 h. In addition, the coatings are resistant to temperature cycling, while the activity of the commercial catalyst decreases under these conditions.

## ACKNOWLEDGMENTS

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