Formation of Ordered Honeycomb-like Structures of Manganese Oxide 2D Nanocrystals with the Birnessite-like Structure and Their Electrocatalytic Properties during Oxygen Evolution Reaction upon Water Splitting in an Alkaline Medium

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ABSTRACT: In this work, a chemical reaction between gaseous ozone and aqueous solution of Mn(CH$_3$COO)$_2$ in drops has been researched. It has been shown that the formation of H$_2$MnO$_3$$\cdot$nH$_2$O nanocrystals with a morphology of nanosheets and a birnessite-like crystal structure with a thickness of 5−8 nm is observed on the surface of drops. These nanocrystals are oriented spontaneously to the solution−gas interface and constitute peculiar ribbons with a width of 1−2 μm, some of which form ordered honeycomb structures (OHS) with a 5−20 μm cell size. To explain the observed effect, the scheme of chemical reactions that take place at the interface between the surface of a drop and ozone has been modeled, and it can be described using a diffusion pattern model taking into account the action of “force fields” on the surface of a drop, which arise due to its curvature. After the drop is dried, these structures practically retain their morphology and form a fractal structure with a geometric area equal to the area of the drop base on the surface of the substrate. The study of the electrocatalytic properties of these structures revealed that they are active electrocatalysts in the oxygen evolution reaction (OER) during water electrolysis in alkaline medium. The most efficient of the obtained electrocatalysts are characterized by an overpotential value of 284 mV at a current of 10 mA/cm$^2$ and the Tafel coefficient of 37.7 mV/dec and are currently one of the best among pure manganese oxides. Finally, it has also been assumed that this effect is explained by the morphological features of the structures obtained, which contribute to the removal of oxygen bubbles from the electrode surface during electrolysis.

INTRODUCTION

As is well known, manganese oxides are frequently used as, for instance, electrode materials for chemical current sources, electrochemical sensors, adsorbents etc. These oxides are also considered as promising noble metal-free electrocatalysts for the decomposition of water by electrolysis. As follows from the analysis of these works, such electrocatalysts allow water electrolysis in the alkaline medium with oxygen evolution reaction (OER) overpotential varying from 340 to 500 mV at 10 mA/cm$^2$ current density. It is well known that studying the oxygen evolution is of vital importance also in connection with searching new catalysts for organic compounds’ oxidation.

A wide range of modern preparative chemistry methods are used for the synthesis of this substance, including the hydrothermal method, solid-state reaction technique, electrochemical deposition, successive ionic layer deposition, sol−gel, precipitation, chemical bath deposition, etc.

The aim of this investigation is the development of an interfacial synthesis method or, rather, a gas−solution interface technique (GSIT). This method is based on the use of sparingly soluble compounds formed after the interaction of a salt dissolved in a liquid with a gaseous reagent supplied to the liquid−gas interface. Previously, GSIT was effectively applied to obtain a plethora of thin films of manganese and iron oxides, as well as arsenic sulfide, lanthanum fluoride, and microtubes based on them.

The principal feature of the experiments described in this work is that salt solution is applied in the form of a drop on the surface of an inert substrate. The relevance of such work is lying in the fact that the processes of planting and evaporating liquid drops are the basis, for example, of two-/tree-dimensional (2D and 3D) printing technologies or methods for producing electrodes of various electrochemical devices, which is called “drop-casting”. During evaporation of solution and suspension drops of various substances, unique conditions can emerge and a number of effects can be observed that lead to the structuring of the resulting products. In particular, one of these structuring effects is named “coffee-ring”.

The experiments carried out in the current work are based on a new technique and compared to well-known ones. Before drying, the surface of a salt solution drop was treated by a...
gaseous reagent according to the GSIT method. The objects for the research are drops of an aqueous solution of Mn(CH₃COO)₂ with a volume of 8–20 µL applied on the surface of glass, single-crystalline silicon, or stainless steel and gaseous ozone. The choice is explained by the fact that this reaction has already been investigated, as a result, it has been shown that in the GSIT conditions during the interaction between Mn(CH₃COO)₂ solution, located in the cell and having a flat interface, and gaseous ozone, a hydrophobic film of manganese oxide (III, IV) is formed on the surface of the solution and after completion of the reaction it continues being localized on it.

The aim of this work was to study the features of these films formed on the surface of Mn(CH₃COO)₂ solution droplets with various concentrations and to study their properties as an OER electrocatalyst for water electrolysis in an alkaline medium.

### RESULTS

The Mn(CH₃COO)₂ solution drops (8–20 µL in volume) having the diameter from 3 to 10 mm were placed on the substrate surface. The contact angle for the glass substrate was approximately 52°, for single-crystalline silicon, 20°, and for stainless steel, this value was ~60°. When such droplets were dried in air, clearly visible rings were formed on the surface of the substrate with diameters corresponding to the diameter of the base of the droplet. Obviously, these rings are formed from crystals of dissolved salt in accordance with the “coffee-ring” effect. However, if the surface of the drops is treated with ozone for 10 min or more before drying, a brown film in the form of round spots with different shades is formed on it. It turned out that such films obtained from solutions with a concentration of more than 0.005 M are weakly bonded to the surface of the substrate and partially crack and separate from it. This occurs, apparently, due to the presence of mechanical stresses in such films and the appearance of forces distorting their planar geometry.

An optical microscopy study of such drops on a glass surface immediately after the reaction showed that a layer of separate bizarre curved “ribbons” is formed on the drop surface. Several images of such ribbons, taken in transmission modes, are shown in Figure 1. As can be seen from these figures, the width of such ribbons is several microns and they form a network of ordered honeycomb-like structures (OHSs) in a number of areas. Part of these structures forms peculiar circles with a diameter of up to 100 µm. This network does not disappear after the drop is dried.

These effects were observed on no less than 2 dozen different samples, but it was not possible to identify a clear effect that characterizes the location of OHS on the spot surface. We can only evaluate the probability of the appearance of such OHS among the common fractal structures for various samples, which is about 10–30%, and it is higher in the center of the spot.

After drying these drops, colored spots remained on the surface of the substrates and then were studied by scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), and Raman spectroscopy. According to the results of SEM analysis (Figure 2) on the surface of droplets of more concentrated solutions, ribbons of a relatively larger width are formed and their density is higher. It is significant that these networks of ribbons practically do not collapse after the droplets dry in air. The width of individual ribbons is 1–2 µm, and they form six- and five-membered OHS meshes a with size of 5–20 µm. It should be noted that in a number of spots, the alternation of six- and five-membered structures is similar to an alternation in the structure of carbon fullerenes or a sequence of fragments on the surface of a soccer ball. From the FESEM images (Figure 3), it can be seen that each of the ribbons consists of separate randomly oriented planar nanocrystals with a thickness of about 5–8 nm. It follows from Figure 3c that the ribbon thickness is about 150 nm.

As follows from the X-ray diffraction data (Figure 4a), nanocrystals are characterized by an X-ray diffraction pattern with peaks at 37.6, 55.0, and 66.0°. These three peaks can be indexed to layered birnessite-like manganese oxide with hexagonal crystalline lattice \( (a = b \approx 5.82, c = 14.62, \text{JCPDS No. 018-0802},) \), also called \( \delta-\text{MnO}_2 \). A birnessite tends to be nanocrystalline, and its hexagonal layer consists of 2D edge-shared \( \text{MnO}_6 \) octahedra (usually \( \text{Mn}^{4+}/\text{Mn}^{3+} \) ions) with different cations and water molecules in the interlayer space. The ratio of \( \text{Mn}^{3+} \) to \( \text{Mn}^{4+} \) as well as the content of \( \text{H}^+ \) and water molecules in the interlayer space is difficult to evaluate, since it strongly depends on the synthesis conditions.
and can vary because of the influence of external factors, for example, during the storage or changing of the solution acidity, etc. Since no other cations could be included in the structures obtained by GSIT, we can identify the formula of the synthesized compound as $\text{H}_2\text{MnO}_2$. This is also proved by Raman spectrum of a substance in Figure 3b, where peaks at 292, 505, 575, 654, and 737 cm$^{-1}$ belong to $\text{H}_2\text{MnO}_2$ with a crystalline structure similar to birnessite. According to ref 38, the presence of peaks at 505, 575, and 654 cm$^{-1}$ indicates a crystalline structure with many defects that determine the high electrocatalytic activity in OER.

Electrocatalytic properties of the synthesized layers were analyzed using the solutions with concentrations of 0.0015, 0.003, and 0.005 M and treatment time of 10 min. The best electrochemical characteristics in the OER during alkaline electrolysis of water had a sample obtained using a solution with a concentration of 0.003 M (Figure 5a). As follows from it, it is characterized by the lowest overpotential value of 284 mV at 10 mA/cm$^2$. An important parameter characterizing the microkinetics of catalytic processes in OER is the Tafel slope, which can be measured as the current density logarithm versus overpotential, and for the last noted sample, its value is equivalent to 37.7 mV/dec (Figure 5b). Apparently, for this sample, OHS of manganese oxide with optimal parameters for electrocatalysis is formed on the surface of the substrate.

**DISCUSSION**

In our opinion, when a drop of solution is treated with ozone, the following sequence of interactions occurs on its surface. Thus, the first stage is a redox reaction between ozone molecules of the gas phase and Mn(II) cations on the solution surface

$$\text{Mn(CH}_3\text{COO)}_2 + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{MnO}_2 \cdot \text{nH}_2\text{O} + \text{CH}_3\text{COOH}$$

It is important to mark that CH$_3$COOH molecules are formed in this reaction, which are removed from the solution as the droplets dry. The other reaction products are hydrophobic seeds of $\text{H}_2\text{MnO}_2 \cdot \text{nH}_2\text{O}$ nanocrystals, which at a given neutral pH value of the solution have a negative charge and therefore repel each other and form a layer of nanoparticles at equal distances on the solution surface. After a while, there is a diffusion of ozone molecules into the salt solution through the surface free of nanocrystals and they start to grow from the solution side, due to which they become larger. The formation of such nanocrystals is promoted by convection flows, which are known to be observed in a drop during its drying and contact with air. This process, in turn, leads to mixing of a solution of Mn(CH$_3$COO)$_2$ and aligning of its concentration in the whole volume of a drop.

From our perspective, $\text{H}_2\text{MnO}_2 \cdot \text{nH}_2\text{O}$ nanocrystal growth at the interface between the drops and air can be described by taking into account the diffusion pattern model, which describes the fractal growth of crystals under the conditions when chemical reactions and the process of diffusion of reagents into the reaction zone simultaneously take place. Such conditions are the most convenient for ordered periodic arrangement in space of the chemical reaction products.

It can also be assumed that during the formation of the honeycomb-like structures, the forces that arise on the surface of the drop due to its curvature play a paramount role. Such forces include both the force of gravity, which promotes the movement of nanocrystals “down the slope” of the drop surface, and the force of convection flows arising inside the drop and on its surface during partial evaporation. These additional interactions on the surface of the drop form unique force fields that lead to the formation of the ordered honeycomb-like structures with a minimum energy. The hypothetical model of OHS formation is shown in Figure 6.

In general, we should point out that the results obtained exceed the analogic electrocatalytic characteristics of similar composition catalysts, synthesized by other methods (Table 1). As one can see from this table, the closest values of the overpotential of 343 mV and the Tafel coefficient of 43.6 mV/dec has the $\text{MnO}_2$ with carbon dots incorporation, but these values are worse than achieved in the current work. Apparently, this is due to the unique morphological features of the
by incorporating H substances into the interlayer space of metal hydroxides or catalytically active metals, by intercalation of various particularly, by doping the nanocrystals with various electro-properties of such materials can be further improved, optimal electrochemical characteristics. Undoubtedly, the electrocatalyst samples allows us to choose the samples with concentration and therefore obtaining a series of similar synthesis. For instance, changing the Mn(CH₃COO)₂ solution method is the possibility to set precisely the conditions of the morphology, these structures on the surface of stainless steel during electrolysis of water in alkaline conditions. There is no doubt that these OHSs have a number of other practically application, for example, as electrodes in the form of oxygen evolution reaction. The best of the obtained electrocatalysts is characterized by an overvoltage value of 284 mV at a current of 10 mA/cm² and a slope of the Tafel coefficient of 37.7 mV/dec, which is currently among the best for manganese oxides. The morphological features of the synthesized structures, which during electrolysis contribute to the removal of oxygen bubbles from the electrode surface, apparently explain these properties.

■ METHODS

Synthesis of the Ordered Honeycomb-like Structures of Manganese Oxide. Mn(CH₃COO)₂ (analytical grade from Vecton) is one of the reagents. Aqueous solutions were prepared using Milli-Q high-purity water with resistivity approximately 18 MΩ·cm. Plates of a glass or single-crystalline silicon with size 20 × 20 × 0.3 mm³ and plates of stainless steel (8 × 20 × 0.5 mm³) were used as the substrates. Before synthesis, these plates were treated in an ultrasonic bath filled with a solution of acetone for 20 min. After that, plates of glass were placed into a diluted KOH solution (pH = 9.5), kept there for 30 min, washed with water, and dried in air at room temperature. Single-crystalline silicon wafers were etched in concentrated HF for 15 min and then washed in distilled water multiple times to remove the excess acid. After that, they were treated for 20 min with a mixture of 3% H₂O₂ and NH₄OH solutions with pH ~ 9.5, washed with water, and dried in air. Stainless steel plates were polished using abrasive paper, treated in an acetone ultrasonic bath for 20 min, washed, and dried the same way as mentioned above.

Table 1. Comparison of Overpotential and Tafel Slope Values for Electrodes Based on Manganese Oxides

| electrocatalyst | synthesis method | substrate | overpotential (mV) at current density 10 mA/cm² | Tafel plot (mV/dec) | ref
|----------------|-----------------|----------|-----------------------------------------------|--------------------|-------|
| H₂MnO₄·nH₂O | GSIT           | Ti       | 284                                           | 37.7               | this work |
| Mn₃O₄ and α-MnO₂ | electrochemical method | Ti       | 570                                           | 106                | 10     |
| tube-in-tube nanostructure of MnO₂@TiO₂ | chemical bath deposition | Ti foil   | 501 mV at 20.87 mA/cm²                  | 43.6               | 12     |
| carbon dots–MnO₂ | simple microwave-assisted hydrothermal method | glassy carbon electrode | 343                                           |                     |       |
| α-Mn₃O₄ | Galvanostatic deposition | FTO      | 350 mV at 0.24 mA/cm²                 |                     | 13     |

When ozone interacts with the surface of Mn(CH₃COO)₂ solution droplets, planar nanocrystals of manganese oxide Mn(III, IV), with a thickness of 5–8 nm and a crystal structure similar to birnessite, are formed on it. These nanocrystals are spontaneously oriented along the solution–gas interface and form peculiar ribbons with a width of 1–2 μm, some of which form ordered honeycomb-like structures with a cell size of 5–20 μm. This effect can be explained using a diffusion pattern model taking into account redox reactions and reagent diffusion in the layer on the drop surface, resulting in the formation of nanocrystals of the above-noted composition and structure. As the reaction proceeds, these nanocrystals fall into additional force fields on the droplet surface and, as a result, “fit” into ordered structures. After the drop is dried, they retain their morphology and form a fractal structure on the surface of the substrate with a geometric area equal to the area of the drop base. The study of the electrocatalytic properties of these structures on the surface of stainless steel depicted that they are active electrocatalysts for the oxygen evolution reaction during electrolysis of water in the alkaline solution. The best of the obtained electrocatalysts is characterized by an overvoltage value of 284 mV at a current of 10 mA/cm² and a slope of the Tafel coefficient of 37.7 mV/dec, which is currently among the best for manganese oxides. The morphological features of the synthesized structures, which during electrolysis contribute to the removal of oxygen bubbles from the electrode surface, apparently explain these properties.
The synthesis procedure consists of several steps. First of all, Mn(CH3COO)2 solution drops with a concentration of 0.001–0.1 M were planted on the surface of substrates and then placed in a flow reactor with a diameter of 20 mm, into which a mixture of air and ozone was supplied. The air flow rate was 30 l/h. Ozone was produced by barrier-type pulse generator OZ-1 M with an ozone output of 0.4 g/h. The time of the sample treatment ranged from 1 to 10 min.

Characterization. As a result of the reaction with ozone, a light brown film was formed on the surface of the drops, and after drying, it was studied by SEM, Raman, and X-ray diffraction techniques. Important information was obtained via optical microscopy using a Biolam microscope (manufactured by LOMO) equipped with an Almeria digital camera, taking images in transmission modes. Here, micrographs of drops surface after its interaction with ozone as well as after drying it was formed on the surface of the drops, and a He–Ne laser as the excitation source and power of 0.018 mWt, where accumulation time was 600 s. Electron micrographs were obtained with microscopes Zeiss EVO-40EP and Zeiss Auriga. X-ray diffraction analysis was performed on a Bruker D2 Phaser diffractometer equipped with a Cu Kα X-ray source. Raman spectra were obtained using a LabRAM HR 800 spectrometer (Horiba Jobin Yvon) with a Ne laser as the excitation source and power of 0.001 mWt, where accumulation time was 600 s.

Electrochemical Characterization. Electrochemical experiments were conducted at room temperature using a standard three-electrode cell connected to an Elins P-30I potentiostat. A stainless steel plate with a spot of manganese oxide with a diameter of 3 mm was used as the working electrode. Platinum foil and Ag/AgCl (aq. KCl sat.) electrode were used as the counter electrode and as the reference electrode, respectively. The electrolyte was 1 M KOH solution (pH = 13). Polarization curves were acquired at a scan rate of 5 mV/s. Electrochemical measurements were made with iR compensation. The overpotential was converted from the Ag/AgCl electrode scale to a reversible hydrogen electrode (RHE) scale according to Nernst eq 2

$$E_{\text{RHE}} = E^0_{\text{Ag/AgCl}} + 0.059 \text{pH} + E_{\text{Ag/AgCl}}$$

(2)

where $E^0_{\text{Ag/AgCl}}$ is the standard potential of the Ag/AgCl electrode and $E_{\text{Ag/AgCl}}$ is the potential of the Ag/AgCl electrode, obtained by measurement. Equation 3 was used to calculate the Tafel coefficient.

$$\eta = b \cdot \log (j)$$

(3)

where $b$ is the Tafel coefficient, $\eta$ is the overpotential, and $j$ is the current density. The last one was calculated with respect to the electrocatalyst area on the electrode surface.

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