Запропонований сітчастий цинковий противелектрод для створення електрохромного пристрою з можливістю рекуперації електричної енергії, витраченої на процес затемнення. Пошук відповідного режиму формування цинкового сітчастого електрода необхідної ємності реалізовували за допомогою декількох підходів: використання багатожильних основ, осадження цинку з різних типів електролітів, використання намазних електродів активною масою різного складу. Осадження цинку з простого сульфатного електроліту дозволяло одержати хороші осади, однак такий електрод не забезпечував необхідної ємності. Цинкові осади, отримані з лужного цинкатного електроліту, мали розвинену поверхню і велику ємність, але при цьому спостерігалось осипання цинку, значне збільшення товщини електроду і темний колір осаду. Намазний електрод з пастою на основі оксиду цинку, графіту і полівінілбутіралю показав найкращу ємність – 0,83 мА·год. Запропонований спосіб формування сітчастого цинкового електрода використаний для розробки електрохромного пристрою з можливістю рекуперації електричної енергії.

Прототип, зібраний з намазними електродами, демонстрував стабільні характеристики при глибині затемнення – 50 %. Показана можливість рекуперації електричної енергії шляхом використання електрохромного пристрою як хімічного джерела струму при його розряді на активний опір у вигляді світлодіоду

Ключові слова: електрохромний пристрій, гідроксид нікелю, полівінілбутираль, цинк, цинкат, цинковий електрод, рекуперація, хімічне джерело струму, розряд, заряд

SELECTION OF THE FORMATION MODE OF A ZINC MESH ELECTRODE FOR AN ELECTROCHROMIC DEVICE WITH THE POSSIBILITY OF ENERGY RECOVERY

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1. Introduction

The world's power consumption has been continuously growing over the last decade, and recent analysis has revealed that this trend continues [1, 2]. Under these conditions, aside from the development and introduction of new power sources, another possible route is to decrease power consumption, which can be aided with «smart» smart devices as the can play an active role in saving electricity and material resources [3, 4]. They allow for better optimization of time required for the execution of functional tasks.

One type of such devices is «smart» windows which can reversibly change their optical characteristics – color, transparency, reflectivity coefficient, glossiness.

The use of «smart» windows can reduce the power consumed for air conditioning, which is especially relevant when considering constantly increasing annual average temperature across the world. They can also allow for less power consumed during «peak» periods. The roadblock for wide adoption of the device into construction and other industries is their

high cost. According to different sources, their cost is about 200–800 USD/m^2 [5, 6]. It is known that the main reason for such high cost is due to low production value, transferring production upcost into the final product. Another reason is the use of expensive vacuum sputtering methods for layer deposition.

So, on the one hand, there is a potential benefit from the mass adoption of this technology, on the other hand, the significant cost of «smart» windows. Thus, all studies aimed at developing and lowering the cost of this technology are of relevance.

2. Literature review and problem statement

A thing to note is that the majority of studies are aimed at improving characteristics (color switching rate, absorbance spectra) by forming nanostructures and nanocomposites [7, 8]. Such approaches require non-trivial reagents and layer formation techniques, thus making such studies difficult to implement for mass production. Despite a large number of published papers on improving specific characteristics

of electrochromic films or electrochromic devices as a whole, most of the proposed technologies cannot be introduced due to high cost or impracticality.

Nevertheless, there are few studies aimed at reducing production costs of electrochromic devices. The paper [9] proposed a simple electrochemical technology – cathodic template deposition of $Ni(OH)_2$-PVA film. The film deposited in this way had strong adhesion to the substrate and good electrochromic characteristics. In [10], the same film was deposited on a pretreated substrate, which resulted in more uniform films with improved electrochromic characteristics. The pretreatment consisted of «soft» etching of the conductive substrate. «Soft» electing was done electrochemically in 1 M HCl. Such treatment roughened the substrate surface on the nanolevel and altered the properties of the FTO layer, improving its wettability by the electrolyte.

To reduce the cost, the authors [11] proposed the design of the electrochromic device, where one of the electrodes was replaced with electrochemically active mesh. The proposed design of the device was positioned for installation in the upper parts of view and light windows. At the same time, it was found [12] that the most suitable material for a mesh counter electrode is silver. However, it was also found that zinc can also be used.

It should be noted that [11] also showed a successful example of a device with a mesh electrode consisting of copper wire coated with a thin layer of galvanic silver. However, when using such materials, it is virtually impossible to recover at least part of the electricity used for coloration. This is due to the fact that the potential difference between nickel oxide and silver electrode is rather small, and during bleaching the polarity is reversed.

On the other hand, there is an active development of electrochromic power sources. The papers [13, 14] describe the successful use of electrochromic devices with flat parallel electrodes as chemical power sources. Considering that the thickness of electrochromic electrodes is usually below 1 μm [15, 16], their effectiveness is high and they can be used as electrochromic supercapacitors.

The zinc electrode can be a suitable candidate for the mesh electrode in the $Ni(OH)_2$-based electrochromic device [12]. The standard electrode potential of $NiOOH/Ni(OH)_2$ is +0.49 V, and $Zn(OH)_2/Zn$ – 1.245 V [17] (for Zn in alkali saturated with $[Zn(OH)_2]^{2-}$). Thus, the approximate voltage of an electrochromic cell can be about 1.735 V. Under these conditions, cell discharge can be attempted to recover part of the energy spent on coloration.

It should also be mentioned that the zinc electrode is used in Zn-Ag [18, 19] and Ni-Zn alkaline batteries [20, 21]. This indicates sufficient reversibility of such electrode, which is necessary for the electrochromic device.

3. The aim and objectives of the study

The aim of the study is to determine the formation regime for the zinc mesh electrode, which results in the electrode with the highest capacity and the smallest electrode size and use that electrode in the electrochromic device prototype.

To achieve this aim, the following objectives were set:
– to use different methods to form a zinc electrode;
– to study the electrode capacity and find which formation method results in the electrode with the highest capacity;
– to verify the operation of the electrochromic device and its capability as energy storage.

4. Materials and methods used to make zinc electrode and electrochromic device

A square wire electrode was used as a prototype of the zinc mesh electrode. The mesh electrode here refers to a zinc electrode in the form of a frame, which represents a single cell unit of the mesh. Copper wire was used as a substrate for electrochemical deposition of zinc or coated with active mass. The active mass was prepared from a dried mixture of ZnO, graphite (GAK-3) and polyvinyl butyral (PVB). Before deposition, the copper wire was degreased with soda paste, washed with distilled water and ultrasonically cleaned (10 min, 60 W, 41.5 kHz) and dried. Directly before coating, it was treated with 5 % HCl for 5 min. To obtain a relatively flat and developed surface, two electrolytes were used – sulfate and alkaline (zincate). The compositions are listed in Table 1. These electrolytes are traditional for zinc hydrometallurgy and for making zinc powders. It should be noted that deposition with different surface areas was carried out to estimate the effect of this factor on the capacity of the electrodes.

Table 1

Electrolyte compositions for zinc deposition [32]

Electrolyte No. 1 (sulfate)	Electrolyte No. 2 (zincate)
$ZnSO_4 \cdot 7H_2O$ 483.6 g/L (110 g/L Zn^{2+})	ZnO 22.8 g/L, NaOH 280 g/L

Electrolytes for coating Cu wire with Zn.

To increase the electrode area without significantly affecting the wire diameter, the following approach was used. Instead of 0.8 mm wire, 2 or 3 0.4 mm wires were twisted into a single piece. The twist step for all twisted electrodes was 1 twist per 1mm of length. The twisted wire was then bent into a square electrode to model a single cell of the mesh electrode – Fig. 1.
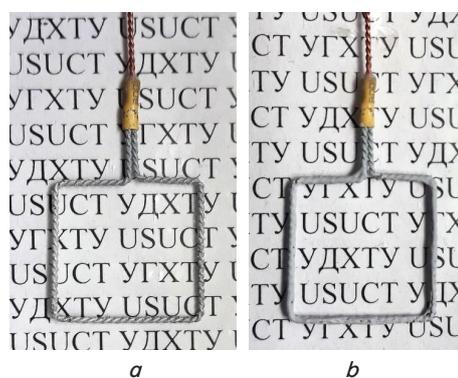

Fig. 1. Photograph of the mesh electrode:
a – copper substrate (2 0.4 mm wires twisted together) with deposited zinc, *b* – copper substrate (2 0.4 mm wires twisted together with deposited zinc and coated with ZnO paste

To further increase the electrode capacity, it was decided to coat the electrode with ZnO paste, which in some cases contained graphite (conductive additive) and PVB binder on the top of the zinc deposit. Before pasting, ethanol was added to the mixture to form a paste, which was then applied to the electrode and allowed to dry for half an hour. The prepared active mass had good adhesion to the substrate and durability. All formation regimes are listed in Table 2.

Table 2

Formation regimes of zinc coating on copper substrate

Descriptions of Cu substrate, number of wires and ∅	Electrolyte and conditions for Zn deposition		Paste mixture (ZnO:graphite:PVB), wt. %	Label
	Sulfate No. 1 [deposition time×layers, current density]	Alkaline No. 2 (zincate) [deposition time×layers, current density]		
1×0.8 mm	8.5 min×2, 300 A/m²	–	no	1-1-0.8S
2×0.4 mm	8.5 min×4, 300 A/m²	–	no	2-2-0.4S
2×0.68 mm	8.5 min×4, 300 A/m²	–	no	3-2-0.68S
3×0.4 mm	8.5 min×4, 300 A/m²	–	no	4-3-0.4S
2×0.4 mm	8.5 min×2, 300 A/m²	4 min×1, 600 A/m²	no	5-2-0.4A6
2×0.4 mm	8.5 min×2, 300 A/m²	4 min×1, 300 A/m²	no	6-2-0.4A3
2×0.4 mm	8.5 min×2, 300 A/m²	4 min×1, 200 A/m²	no	7-2-0.4A2
2×0.4 mm	8.5 min×2, 300 A/m²	4 min×1, 150 A/m²	no	8-2-0.4A1
2×0.4 mm	8.5 min×4, 300 A/m²	–	98:0:2	9-2-0.4SP
2×0.4 mm	8.5 min×4, 300 A/m²	–	82:16:2	10-2-0.4SP

Graphite rods were used as counter electrodes for zinc deposition. Sample morphology was studied using the Carl Zeiss optical microscope (Germany) connected to PC.

Electrochemical measurements.

After formation, electrochemical characteristics of each electrode were evaluated by means of cyclic voltammetry (CV). Measurements were conducted using a 3-electrode cell [22]. Electrodes were cycled from –1500 to –200 mV vs NHE at 10 mV/S. In addition to CV, the capacity of each formed electrode subjected to galvanostatic charge-discharge cycling at 1 mA [11] was evaluated. In cases where the capacity was such that the measurements were too long (hour and more for 1 charge-discharge cycle), the cycling current was increased to 10 mA. Average capacity for 10 cycles was used to evaluate the potential usability of such formation method. Ag/AgCl (KCl ast.) was used as an electrode. Nickel foil was used as a counter electrode. ~0.1 M KOH solution saturated with $K_2[Zn(OH)_4]$ was used as an electrolyte.

Electrolyte preparation: 2 g ZnO was put into a flask and 200 ml of 0.1 M KOH was added. After more than a day, the prepared solution was used as is.

Testing of finished prototypes.

The electrode with the highest capacity was used to make a prototype of the electrochromic device. The electrochromic device was formed using fluorine-doped tin oxide glass (FTO glass, $R<10\ \Omega/\square$, Zhuhai Kaivo Optoelectronic Technology Co. Ltd., China), which was subject to soft electrochemical etching [10]. Working electrode area 2×2 cm, total area 3×2 cm. The composite $Ni(OH)_2$/PVA electrochromic film was deposited using the cathode template method [10]. The prepared half-element was assembled with the zinc mesh electrode and regular glass slide – Fig. 2.

The electrodes were spaced 1 mm apart and the whole assembly was sealed with thermal adhesive along boundaries. A small hole was left, so that the electrolyte, saturated with potassium zincate in ~0.1 M KOH, could be injected. The electrolyte was injected with a syringe and the device was sealed completely. Details about the assembly method and prototype preparation can be found in [11].

Testing of the electrochromic device.

The prototype was subjected to galvanostatic cycling to evaluate optical and electrochemical characteristics. Current values were chosen according to [11] and were +/−1 mA for coloration and bleaching. Electrochemical and optical properties were studied using the setup shown in Fig. 3
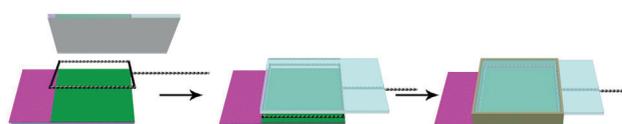

Fig. 2. Electrochromic device assembly.
Colors indicate: ■ — glass, ■ — conductive layer,
■ — composite $Ni(OH)_2$/PVA electrochromic film,
■ — copper wire with zinc deposit, ■ — thermal
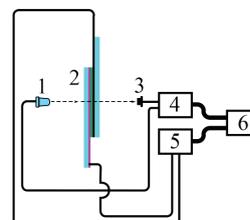adhesive (schematic representation)

Fig. 3. Schematic of the setup for studying electrochromic films: 1 — source of white light (5500 K); 2 — assembled prototype; 3 — photoresistor; 4 — analog-to-digital converter (ADC); 5 — digital potentiostat; 6 — computer

The setup uses the E-154 ADC (Russia) and Elins P-8 digital potentiostat (Russia), along with the standard software package.

To evaluate the possibility of using as a battery, it was connected to a red LED ($U=1.8$ V, $I=3$ mA). Current over time was recorded to evaluate the capacity with real load (LED).

5. Comparison of characteristics obtained for zinc mesh electrode

5. 1. Solution algorithm for set objectives

The priority objective of the present study is to prepare a zinc electrode with the highest capacity. It is also desirable for the electrode size, including wire diameter, to not be affected much. The rationale behind this is that the mesh electrode partially covers the electrochromic electrode, as such device has an opaque region even when fully bleached, which is undesired. High capacity would allow for the mesh with larger cell size, which increases the useful area of the device.

Nevertheless, the necessary minimum capacity of the mesh electrode for coloration and bleaching was found to be 0.04 mA·h per 4 cm² of the working area of the electrochromic film (2×2 cm). This value is determined by the maximum capacity required for the coloration of 4 cm² composite Ni(OH)$_2$/PVA electrochromic film [10].

To increase the actual electrode surface (and thus capacity) while maintaining apparent size and proportions of the zinc mesh electrode, the following steps were done:

1. Instead of a single wire, several wires were twisted together.

2. Instead of sulfate electrolyte, which produced rather flat Zn deposits, the alkaline electrolyte was used, as it produces dendrite deposits with high surface area.

3. Varying deposition current density.

4. Use of additional active material layer with different compositions.

5. 1. Electrochemical characteristics of zinc electrode formed in different ways

Cyclic voltammetry was used for preliminary evaluation of the formed electrode. The primary focus was on the height of the anodic and cathodic peaks, which characterize oxidation and reduction reaction of zinc:

$$Zn+2OH^-\rightarrow Zn(OH)_2+2e^-, \qquad (1)$$

$$Zn(OH)_2+2e^-\rightarrow Zn+2OH^-. \qquad (2)$$
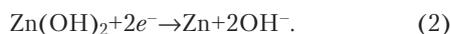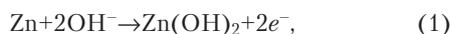
Since the peak height is proportional to the area, the peak height can serve as an indicator of electrode capacity. Peak potential values were also compared, along with the hydrogen part of the curve, to the left of the cathodic peak.

Fig. 4 shows cyclic voltammetry curves for the first four variants of the formed zinc electrode, which differ in the number of twisted wires and deposited zinc layers.

Analysis of the curves suggests that the area of the electrodes plays an important role. And with two larger diameter wires or three wires (sample 3-2-0.68S and 4-3-0.4S) for the electrode frame, the capacity increases in comparison to the frame with a single wire or two smaller ones. Notably, the first cathodic peak of all samples in this series is significantly higher than in subsequent cycles. It can also be observed that some curves have several anodic peaks. Considering that evaluation calculations from CV revealed small numbers, it was decided to develop the electrode surface by depositing zinc dendrites. This can be achieved by using the alkaline electrolyte, the composition of which was described previously.

Thus, the CV curves for the second series of the samples revealed a significant increase in the peak height, meaning higher capacity – Fig. 5, a. However, zinc deposited in such a way had a very developed surface and was falling off from the electrode during transfer. Thus, another series of experiments was conducted with varying zinc deposition current. The rest three CV curves were obtained from the electrodes formed at different current densities (Fig. 5, b–d). Despite the lower particle size at lower current densities, a part of zinc was still falling off, although less intensively. The decrease of the particle size at a lower current density was observed with the help of an optical microscope.
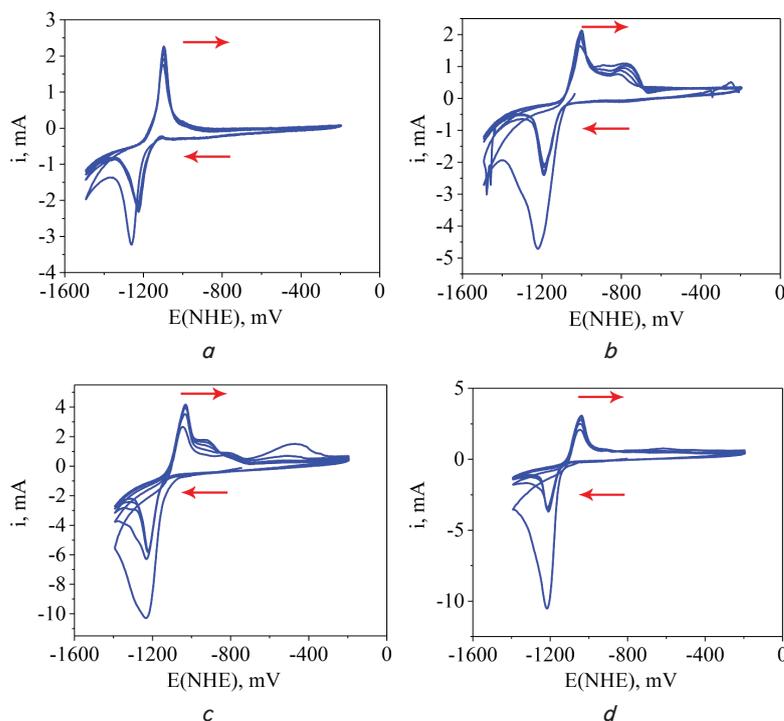
Fig. 4. Cyclic voltammograms (CV) of samples:
a − 1-1-0.8S; b − 2-2-0.4S; c − 3-2-0.68S; d − 4-3-0.4S. Red arrows indicate scan direction
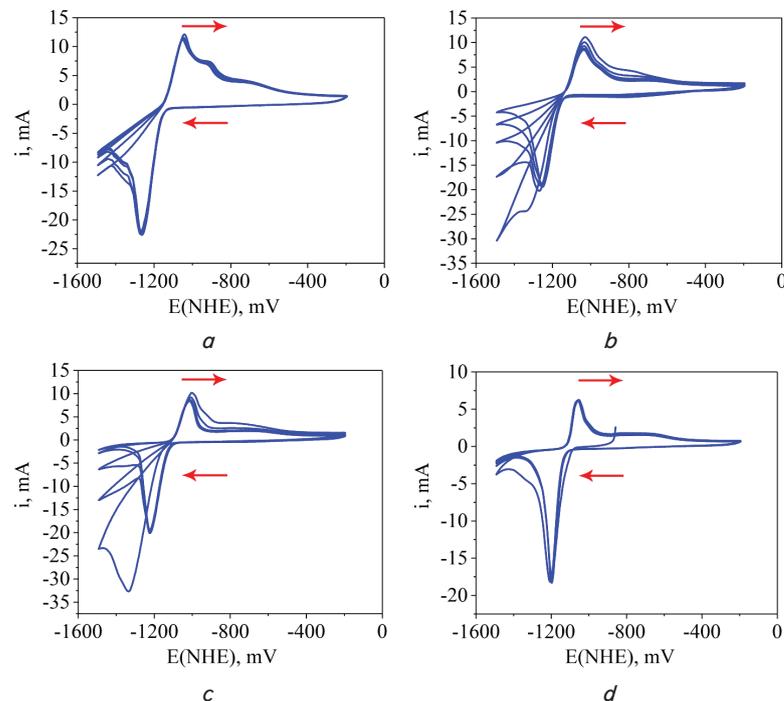
Fig. 5. Cyclic voltammograms (CV) of samples:
a − 5-2-0.4A6; b − 6-2-0.4A3; c − 7-2-0.4A2; d − 8-2-0.4A1. Red arrows indicate scan direction

Analysis of the obtained CV curves allows concluding that the idea to develop the electrode surface was correct, as electrode capacities increased, as evidenced by increased anodic and cathodic current densities. The peak positions remained the same.

Estimated capacities were sufficient for it to be used. However, due to zinc falling off, even at lower deposition current densities, such formation method was deemed impractical. Additionally, formed zinc dendrites also visually increased the electrode thickness, which isn't quite suited for the set goals.

Surface comparison of zinc electrodes formed from different electrolytes is shown in Fig. 6. Morphology images reveal visible differences.

Thus, the zinc deposit from sulfate appears to be continuous, without notable irregularities and of light color – Fig. 6, *a*, *b*. While the deposit from the alkaline electrolyte is dark gray and is composed of fern-like zinc – Fig. 6, *c*, *d*.

Further capacity increase was proposed to realize as it is done in existing batteries, which employ pasted electrodes [23–25]. The paste was composed of zinc oxide with additives.
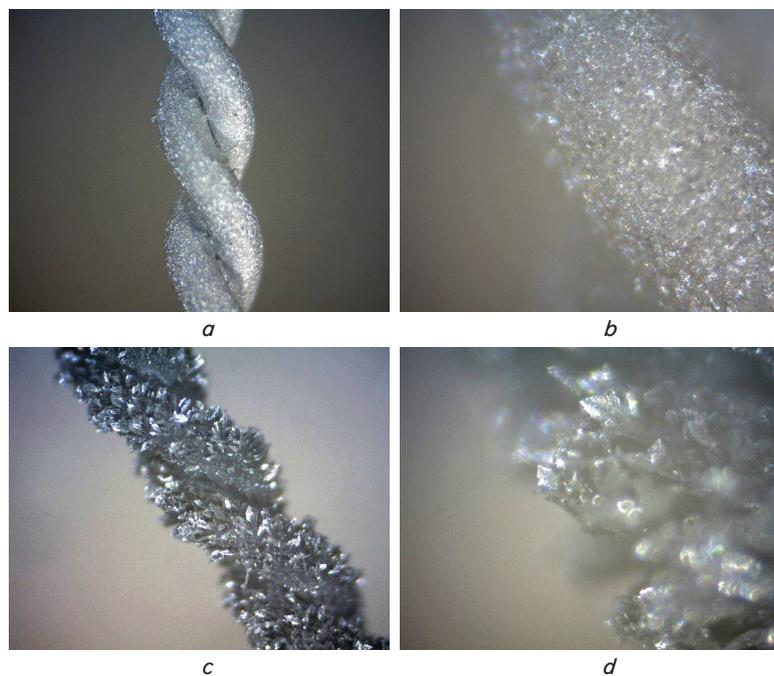
The CV curves of these electrodes are shown in Fig. 7. The electrodes differ by the presence or absence of graphite, the content of which was chosen to be 16 % similar to [26, 27]. Comparison with the previous CV curves shows a significant increase in peak height to 40–140 mA. While electrodes with dendrite zinc from the alkaline electrolyte topped out at 5–13 mA. And deposits from the sulfate electrolyte had even lower currents: 2–10 mA.

It should be mentioned that during the operation of pasted electrodes, gradual material development is observed. In addition, the amount of active mass on both electrodes was similar, which characterizes graphite as an additive that increases capacity.

5. 2. Capacity characteristics of zinc electrode formed by different methods

The electrodes were subjected to galvanostatic charge-discharge cycling to evaluate their capacities under conditions close to real operation. The capacity was averaged from 10 cycles. The calculated data were compiled into a histogram shown in Fig. 8.

Fig. 6. Optical microscopy images of samples:
a, *b* – 2-2-0.4S (80x and 350x, respectively);
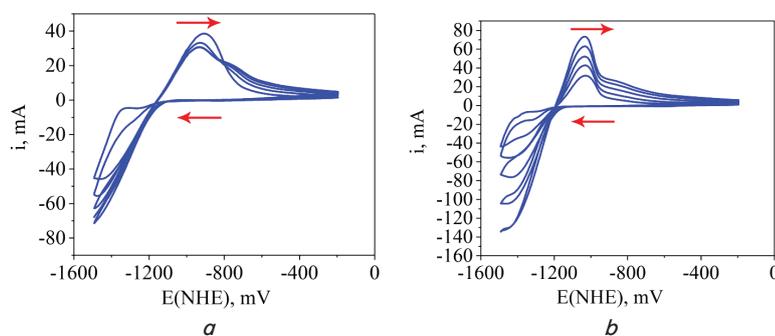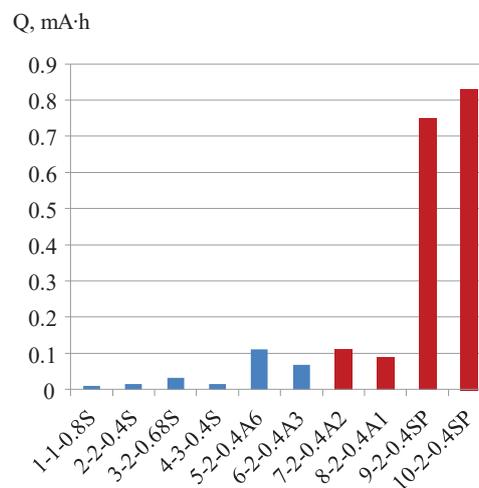*c*, *d* – 5-2-0.4A6 (80x and 350x, respectively)

Fig. 8. Averaged capacities of electrodes prepared in different ways: blue shows the capacities from galvanostatic charge-discharge cycling at 1 mA; red shows the capacities from galvanostatic charge-discharge cycling at 10 mA

It should be mentioned that electrodes with the highest capacities were cycled at 10 mA to shorten the experimental time. The rest were cycled at 1 mA. 1 mA was used as a working current in a similar prototype [11].

Analysis of Fig. 8 reveals that each of the methods used resulted in a capacity increase, namely: transition from deposits with small irregularities to deposits with high surface area and further transition from metal zinc to pasted zinc.

The capacities of the first four electrodes (from left to right) are insufficient for application, as they are below the set minimum of 0.04 mA·h. The highest capacity in this series is observed in the sample 4-3-0.4S and is 0.032 mA·h.

Further modification of the formation method yields the necessary capacity – the capa-

Fig. 7. Cyclic voltammograms of samples:
a – 9-2-0.4SP; *b* – 10-2-0.4SP. Red arrows indicate scan direction

city of all electrodes exceeds 0.04 mA·h. The highest capacity is observed for the sample 7-2-0.4A2 and is 0.11 mA·h. However, deposited zinc falls off easily, which makes such electrode rather impractical to handle.

The last formation variant with the use of pasted zinc electrode yields the necessary capacity and even exceeds it 20 times. The sample with the paste containing graphite has a capacity of 0.83 mA·h, which is more than 20 times higher than required – Fig. 8 (10-2-0.4SP).

A prototype of the electrochromic device with recuperation capability was assembled using the zinc mesh electrode formed by depositing zinc from the sulfate electrolyte onto the 2×0.4 mm copper substrate and coated with ZnO, graphite and PVB (sample 10-2-0.4SP).

5. 3. Test results for electrochromic device prototypes with zinc mesh electrode in coloration and battery regimes

An electrochemical element was assembled to evaluate the functionality of $Ni(OH)_2$-PVA in pair with the zinc electrode in the zincate-saturated alkaline electrolyte. The electrochemical element was galvanostatically cycled at $+/-1$ mA. The coloration bleaching curves of the first 10 and last 30 cycles are shown in Fig. 9.

T, % is transparency, which changes over time (x axis).

During the first 10 cycles, controlled working through the electrodes occurs. This can be observed by working through the electrochromic electrode – Fig. 9, a.

Limit coloration depth was set at about 50 %, which was not exceeded to prevent possible peeling off of the film from the substrate. The coloration degree is assumed as the difference between T (%) for bleached and colored states.

To demonstrate the possibility of recuperating capacity spent on the coloration of the electrochromic element, it was colored at 1 mA, and then an LED was connected to it. All changes in color and emission were photographed – Fig. 10.

As can be seen from Fig. 10, when LED was connected to the prototype, it was emitting light. While the electrochromic film was becoming transparent. The capacity recuperation process was repeated about 10 times and the process parameters didn't show any significant changes.
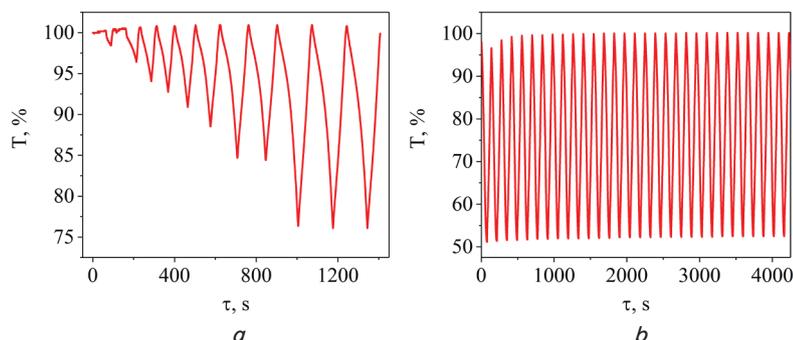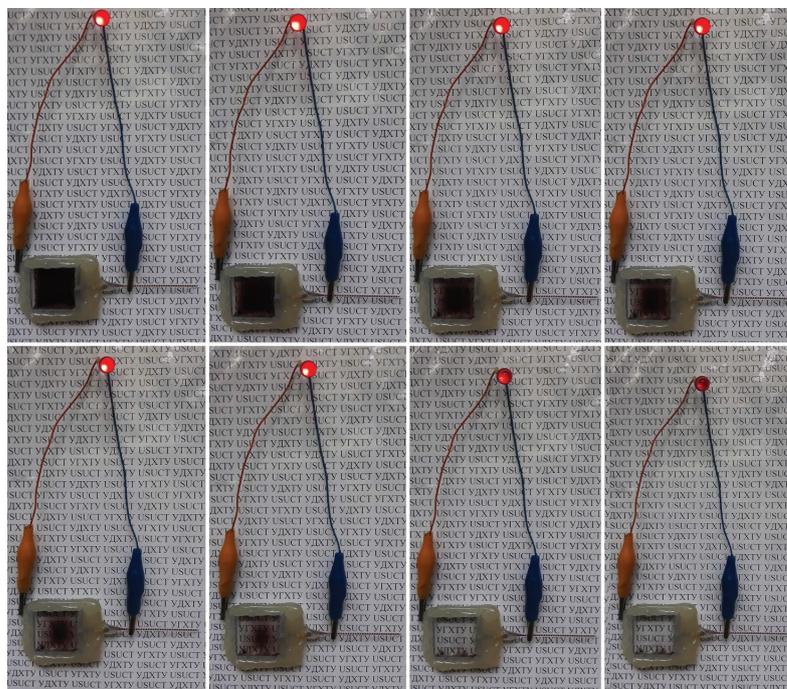

Fig. 10. Photographs of the assembled prototype device with the 10-2-0.4SP zinc mesh electrode and its discharge and bleaching process due to active load (red LED)

6. Discussion of characteristics of zinc electrodes formed by different methods and experimental results for electrochromic device prototype tests

Experiments conducted in this study allowed determining the most promising method of electrode formation. This turned out to be [28] pasting of active mass on the electrode surface.

In turn, the zinc deposit from the sulfate electrolyte is of rather good quality, while the electrolyte is cheap and available [29, 30]. The paste had strong adhesion, did not fall off, and had a good visual appearance and didn't significantly thicken the electrode. After drying, the paste had a light-gray color and after cycling became darker due to the formation of ultrafine zinc particles.

The described method is fast and simple, which is required for reducing the cost of the electrochromic device. Even more, in comparison with the silver mesh electrode [11], the zinc electrode doesn't contain precious metals, is easy to separate from the substrate and recycle.

Additionally, the experiments revealed that the assembled electrochromic element prototype can be used to recuperate part of electrical energy spent on coloration.

Nevertheless, the use of the zinc electrode has drawbacks. During coloration, a small amount of hydrogen can evolve at the zinc electrode. Thus, electrochromic elements will need to be equipped with pressure relief valves, or effective additives will be introduced increasing the polarization of hydrogen evolution.

A promising direction of this research can be search for additives improving the effectiveness of zinc electrode or methods for decreasing its size. It should be noted

Fig. 9. Coloration-bleaching curves of the prototype device with the 10-2-0.4SP zinc mesh electrode: a — cycles 1—10; b — cycles 40—70

that limiting the coloration depth to 50 % ensured that the electrochromic film would not peel off from the substrate. Such limitation prevented the formation of oxygen gas at the anode during coloration, which can be a possible cause for film separation from the substrate. On the other hand, a thicker film can be deposited to improve coloration depth.

In addition, recuperation of electrical energy is important and can result in notable power savings for large windows. Evaluation of scaled up capacity yields the value of about 87.5 mA·h/m^2 of such device [31].

Such amount of electricity can be used to power three bright LEDs for about an hour (assuming current draw of $\approx$20–25 mA per LED, and considering power losses with increasing voltage in step converters to the operating voltage of 3.2–3.6 V).

7. Conclusions

1. The influence of the formation method on the capacity of the zinc electrode was studied. It was found surface morphology had a significant effect on effective capacity.

2. The best electrode in the experimental series turned out to be the electrode formed by depositing a layer of zinc from the sulfate electrolyte onto copper wire and coating it with a ZnO:graphite:PVB paste – 82:16:2. The electrode formed in this way was compact, didn't fall off and had a capacity of 0.83 mA·h.

3. The electrochromic device prototype was found to be stable during coloration-bleaching cycling at +/−1 mA. The prototype was also capable of working as an energy storage unit and was used to power an LED. A possible specific recuperation capacity was evaluated as 87.5 mA·h/m^2.

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