У представленому дослідженні запропонована зміна конструкції комірки для зменшення ціни електрохромних пристроїв. Модифікація конструкції електрохромного пристрою полягає у тому, що замість одного з електрохромних шарів та відповідного електропроводного шару вводиться сітчастий металоокисний електрод. Даний варіант електрохромного пристрою запропоновано використовувати в світлових вікнах та у верхніх частинах оглядових вікон.

Для запропонованого сітчастого електроду були обрані декілька електрохімічних систем, що можуть бути потенційно використані, а саме: $Cu|Cu_2O$, $Zn|ZnO$, $Ni|NiO$ та $Ag|AgO$. Методом циклічної вольтамперометрії були визначені робочі параметри обраних систем – робочі вікна потенціалів та питомі густини струмів піків. З урахуванням отриманої інформації було визначено найперспективніший з них, яким виявився срібляний електрод.

Обраний електрод досліджували методами циклічної вольтамперометрії та у гальваностатичних режимах. У результаті було показано, що питома ємність срібляного електроду мало залежить від густини струму окислення та відновлення. Визначено максимальну та мінімальні питомі ємності досліджуваного електроду, які у 0,1 М розчині КОН складали 0,075 мА·год/см^2 (циклічна вольтамперометрія) та 0,082–0,042 мА·год/см^2 (гальвонстатичні режими). Додатково було показано, що під час електрохімічного циклування у 0,1 М КОН на електроді мають місце наступні перетворення $Ag \leftrightarrow Ag_2O$ та $Ag_2O \leftrightarrow AgO$.

За результатами дослідження при питомий ємності основного (електрохромного) електроду 0,011 мА·год/см^2 запропоновано використовувати сітку з коміркою 2 на 2 см та діаметром проволоки 0,5 мм. Для зменшення вартості сітки було показано, що замість чистого срібла, як матеріалу сітчастого електроду, можна використати мідну проволоку з тонким шаром покриття з гальванічного срібла

Ключові слова: $Ni(OH)_2$, гідроксид нікелю, електрохромний пристрій, сітчастий електрод, протиелектрод, срібло, оксид срібла, питома ємність, світлові вікна

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MATERIAL SELECTION FOR THE MESH ELECTRODE OF ELECTROCHROMIC DEVICE BASED ON $Ni(OH)_2$

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1. Introduction

“Smart windows” are devices that can controllably alter their optical properties: transparency, color, transmittance and reflection coefficient. The core of these “smart windows” are electrochromic films, in which electrochemical reactions occur. During these reactions, transparent forms become colored [1].

“Smart windows” can have various applications. For instance, they can be used in construction, aviation and automobile industries to provide visual control. They can also be used in hospitals for patient examination rooms and also to create a private atmosphere in business centers and meeting rooms [2].

However, the main advantage of “smart windows” is power saving due to lower interior heating. As a result, less power is required for air conditioning. These windows would also lower power consumption in “peak” periods and for lighting [3]. Thus, the use of “smart windows’ should be profitable and widespread, but the reality is different. The high cost of 100 [4] and even up to 400 US $ per square meter [5] negates all advantages of their use. Therefore, the search for technologies that would lower their cost becomes key for the scientific field.

2. Literature review and problem statement

It is known that the use of horizontal (light) “smart windows” results in the greatest power saving among all possible window orientations [6, 7]. This is because direct sunlight passes through them during almost the whole day. Such windows are used in modern apartments located on upper floors, in trade centers, business centers, airports, railway stations, etc. However, because their purpose is to create natural lighting, the requirements to light transmittance are less strict.

The structure of electrochromic windows is shown in Fig. 1. As can be seen from this illustration, an assembled electrochromic device is a package that consists of oxide or hydroxide layers of different metals [8, 9]. As for the electrolyte, the most common is polypropylene carbonate with dissolved $LiClO_4$ [10, 11]. It should be noted that solid electrolyte can also be used. The most common solid electrolytes are oxides of tantalum, zirconium, etc. [12, 13].

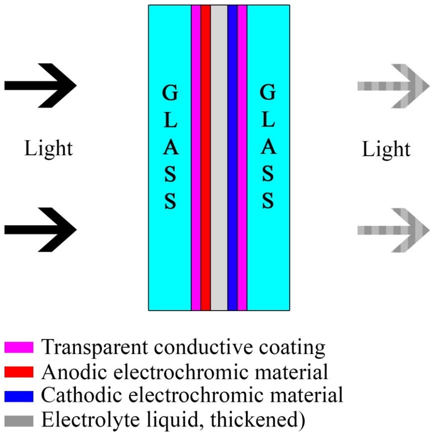


Fig. 1. Cross-section of electrochromic device schematic

For large windows, vacuum sputtering is often used [14]. Considering that material deposition is consecutive, and used materials are different, there are at least 4, 5 in case of the solid electrolyte, separate aggregates. Thus, the cost of the smart window is composed of five separate deposition processes. Because the material thickness is low (usually below 600 nm [15]), the cost of an individual layer is defined by the cost of its deposition process. For vacuum sputtering, the cost is estimated as 8 US $ per square meter [16]. Based on this, the cost of one square meter of “smart window” would be at least 32–40 US $. Considering the cost of assembly, installation of current collectors and their cost, and also two glass panes, electrolyte and control electronics, the minimum cost would be 20–30 dollars more, according to our estimation. So, the total cost could reach at least 70 US $. This number is in agreement with the literature [4], according to which, the cost is estimated from 100 and more US $ per square meter. Considering all this, the main goal of scientific groups should be development towards lowering the manufacturing cost by changing the design, using new and/or cheaper deposition methods.

One possible way to reduce the cost is to replace one of the electrochromic layers along with the corresponding conductive layer (Fig. 1) with a perforated opaque electrode. One of such materials can be a mesh with a large cell size, the material of which is electrochemically active (Fig. 2).

In this case, the manufacturing cost would be lower by the difference between the mesh cost and the cost of vacuum deposition of two layers. If such electrode can also operate in water electrolytes, cost reduction would be even greater. This is because the water-based electrolyte is significantly cheaper than the lithium perchlorate and polypropylene carbonate electrolyte. On the other hand, the disadvantage of such design is the presence of opaque parts. This limits the application of such windows. However, they are suitable for light windows or upper parts of view windows (Fig. 3).

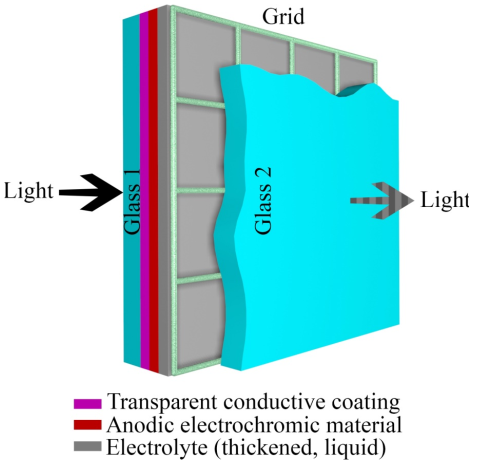


Fig. 2. Design of electrochromic “smart” window with mesh electrode

Fig. 3. Possible application for electrochromic “smart” windows with mesh electrode. Red outlines possible installation places

For the chosen design, mesh material is very important. This can be metallic mesh, the material of which partakes in electrochemical reactions, with oxidized and reduced forms staying at the electrode in the solid state.

It should be noted that the mesh electrode does not impose limitations for designers, and depending on interior (exterior), it can be realized in different forms. For instance, Fig. 4 shows a few possible patterns.

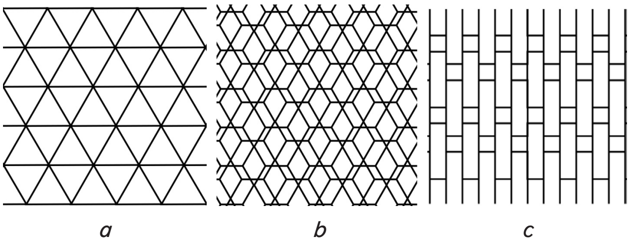


Fig. 4. Possible patterns of mesh electrode:
a – variant 1; *b* – variant 2; *c* – variant 3

$Ni(OH)_2$ based electrochromic electrode operates in basic media [17, 18], with a solution being 0.1 KOH [19, 20]. Therefore, the mesh material should also be chosen with consideration for that. It should be noted that mesh material should have a capacity no lower than that of the electrochromic electrode [21]. Otherwise, two cases are possible: incomplete coloration of the electrochromic electrode or gas evolution due to electrolyte deposition at the mesh electrode. Both variants impede the operation of the electrochromic device and in total are unacceptable. Therefore, the material of the mesh electrode should fit into the following criteria:

1) specific capacity of the mesh electrode should be as high as possible;
2) the electrode should operate in alkaline media;
3) oxidized and reduced forms should be solid;
4) the electrode should operate reversibly.

Considering these criteria, analysis of suitable materials lead to the preliminary choice of several systems: $Cu|Cu_2O$ $Zn|ZnO$ ($Zn|Zn(OH)_2$) [22], $Ni|NiO$ ($Ni|Ni(OH)_2$) [23], $Ag|AgO$ [24] and $Cd|Cd(OH)_2$ [25]. Aside from $Cu|Cu_2O$, all listed electrodes are used in alkaline accumulators, so it can be concluded that their electrode reactions are sufficiently reversible. The copper oxide electrode was chosen, because according to the literature [26, 27], the $Cu|Cu_2O$ pair is sufficiently reversible in 0.1 M NaOH. However, the cadmium electrode was discarded, due to the high toxicity of cadmium, which is greater than that of lead [28].

It should be noted that accumulators employ concentrated alkali – 4 M or higher, as KOH (NaOH) solution. The active material of the electrodes is in powder form with additives. For the electrochromic device, the idea is to employ existing oxide layers on the surface of Ni, Zn and Cu. In case of Ag, the oxide can be formed electrochemically over the course of experiments.

Thus, despite the general similarity of the systems used in accumulators and potentially usable in mesh electrodes, there are a few differences:

1) use of dilute alkaline solution (0.1 KOH);
2) use of metals, the surface of which is covered with oxide-hydroxide films (Ni, Zn, Cu) or metal, on which such films are formed during experiments (Ag).

Because there is no information on characteristics of these systems under required conditions, the aim was set to evaluate specific capacities and conduct comparative analysis. Such analysis could help to find systems that could potentially be used in the developed design of the electrochromic device (Fig. 2).

3. The aim and objectives of the study

The aim of the study is to evaluate the usability of a few metal oxide electrode systems as a mesh electrode of the electrochromic device.

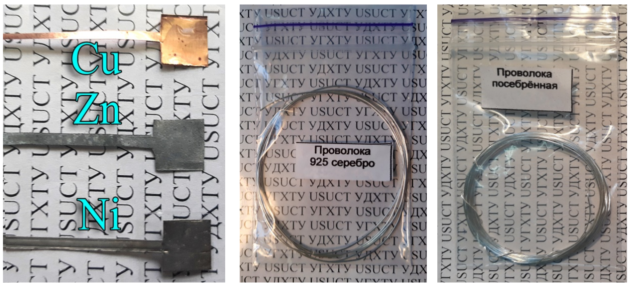
To achieve the set aim, the following objectives were formulated:

– to evaluate specific capacities of a few metal oxide systems in dilute alkali;

– to conduct a comparative analysis of the obtained data, to find the most suitable system for the mesh electrode.

4. Materials and methods used for analysis of metal oxide systems

To evaluate specific capacities of the chosen systems, electrodes made of the corresponding metals were used (Fig. 5). Because we found no silver foil, a 925 silver wire was used instead (Fig. 5, *b*), along with the copper wire coated with a 30 µm thick electrodeposited silver. The wire length was chosen so the working area would match the working area of the square electrodes of Zn, Ni, Cu. The working area of all electrodes was 0.64 cm^2.



a *b* *c*

Fig. 5. Electrodes used in the study: *a* – copper, zinc and nickel foil electrodes; *b* – 925 silver wire; *c* – copper wire with electrodeposited silver

All electrodes were subject to the same pretreatment. The electrode surface was washed with a soda paste and then with distilled water. After that, washed with 99.6 % ethanol and dried. For foil electrodes, one side was masked with a dielectric material.

Electrochemical characteristics were determined by cycling in 0.1 KOH. All tests were conducted using the digital potentiostat Elins P-8 (Russia). The experiments were conducted in the acrylic cell with internal dimensions of 4×2×6 cm. Nickel foil was used as a counter electrode, and Ag/AgCl (KCl sat.) as a reference electrode.

For preliminary evaluation, the materials were studied by means of cyclic voltammetry (CV). CV was conducted at two scan rates – 10 mV/s for the express test, and 1 mV/S for a more detailed evaluation. The data were recorded at 3 points per second.

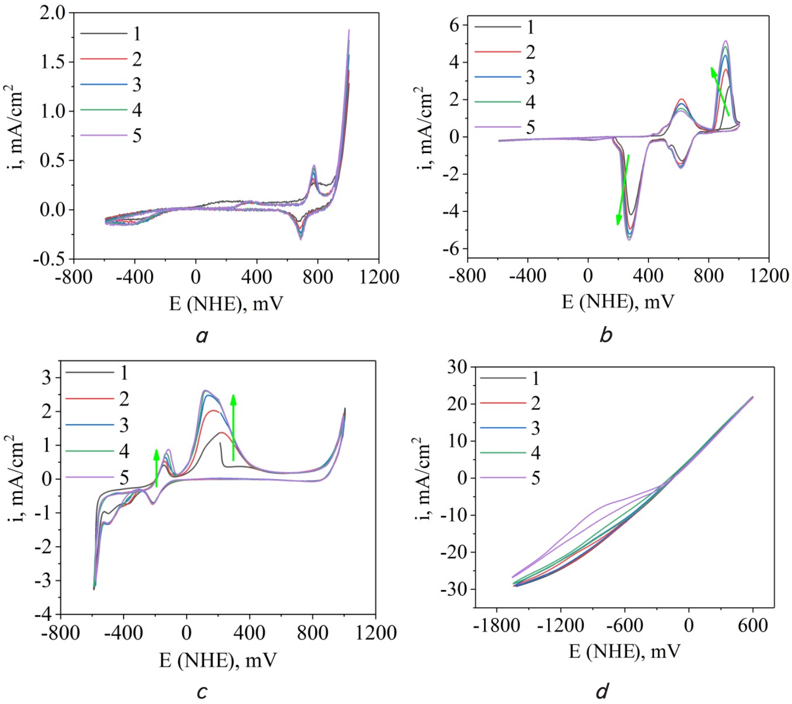
To determine the capacity of the silver electrode by CV curves, a numerical integration was conducted using the trapezoid method along the whole curve considering the sign. Thus, two capacities were obtained for a single curve – cathodic and anodic. Integration was conducted using Microsoft Excel software.

Because CV only allows to approximate capacity, galvanostatic cycling was used for further clarification. Cycling was conducted at current densities of ±2.5, ±5, ±10, ±15, ±20 mA/cm^2. For each current density, 10 cycles were recorded. The capacity was calculated as the average of 10 cycles. The capacity was calculated by multiplying the current density by the reaction time, resulting in a specific capacity in $mA \cdot h/cm^2$ [31, 32].

The morphology of the materials was studied using the Bresser optical digital microscope (Germany).

5. Analysis and comparison of electrochemical characteristics of metal oxide electrodes

To evaluate the electrochemical activity of each electrode, dozens of experiments were conducted to find the working potential window of each material. To reduce time, for this series of experiments the scan rate of 10 mV/s was used. Cyclic voltammograms within the found potential windows are shown in Fig. 6.



a *b* *c* *d*

Fig. 6. Cyclic voltammograms recorded at 10 mV/s for different metals in 0.1 M KOH: *a* — nickel; *b* — silver; *c* — copper; *d* — zinc

The peak height is used to judge if the material is suitable for the mesh electrode. The *x*-axis is the potential. Nevertheless, the potential is related to time through the scan rate. Thus, the graph values of the *x*-axis can be replaced with time. The integral under the curve would be equal to the capacity involved in the process. At the same time, because the peak shape is similar in the first approximation, the peak height can represent the capacity of the electrode during the electrochemical reaction.

Analysis of the CV curves allows to conclude that the behavior of each electrode is different. The nickel electrode demonstrated low peak current densities (Fig. 6, *a*), with peak values not exceeding 0.5 mA/cm^2. From the CV curve of the nickel electrode, it can be seen that oxidation and reduction peak current densities increase during cycling. This is likely due to the fact that although the nickel surface is always coated with oxide and hydroxide compounds [29], during the anodic process, the metallic nickel is electrochemically oxidized. The buildup of oxide and hydroxide compounds results in a gradual increase of current density, as they are electrochemically active. The current increase on the right side of the graph is due to oxygen evolution from water decomposition. In turn, the plateau on the right side is likely related to partial reduction of the remaining oxygen that formed previously.

An interesting picture is observed for the silver electrode (Fig. 6, *b*). The CV curve contains two anodic and cathodic peaks. The height of the outer peaks increases with each cycle. Peak current densities are the highest and reach above 5 mA/cm^2, which is ten times higher than for the nickel electrode. Obviously, the series of anodic and cathodic peaks correspond to $Ag \leftrightarrow Ag_2O$ and $Ag_2O \leftrightarrow AgO$ transformations. It is interesting that, unlike nickel, no significant oxygen evolution is observed at potentials above +1,000 mV, only an insignificant increase of current density. This is likely because of high oxygen polarization on silver oxides.

The copper electrode demonstrated values between those of silver and nickel (Fig. 6, *c*). One of the anodic peaks reached 2.5 mA/cm^2, with others being about 1 mA/cm^2. As in case with silver, two anodic and two cathodic peaks were observed on the CV curve. It is expected that the peaks correspond to $Cu \leftrightarrow Cu_2O$ and $Cu_2O \leftrightarrow CuO$ transformations. It is interesting that there is a growth of anodic peaks, while cathodic peaks remain almost constant. This is likely due to oxidation of metal and formation of the additional oxide film. The growth of anodic peaks with cathodic ones being constant can also indicate instability of this electrode in alkaline media.

In case of the zinc electrode, no peaks were observed on the CV curve. This is likely related to the following explanation. Before experiments, it was assumed that cycling in the dilute electrolyte would occur between $Zn \leftrightarrow ZnO$ or $Zn \leftrightarrow Zn(OH)_2$. ZnO and $Zn(OH)_2$ have low solubility, they should remain on the electrode surface. However, it seems that even in the dilute alkali, zincates are formed, which are quite soluble. Therefore, in the dilute alkaline, constant chemical dissolution of Zn into $[Zn(OH)_4]^{2-}$ occurs. In turn, electrochemical polarization accelerated the dissolution rate (the right side of the curve). High currents on the left part are related to hydrogen evolution at the electrode.

As assumed, for the electrode to start working, ZnO powder was added in order to obtain a zincate-ions saturated solution:

$$ZnO+2KOH+H_2O \rightarrow K_2[Zn(OH)_4]. \tag{1}$$

The solution with zinc powder was kept for a day for equilibration. The solution was then decanted to separate it from remaining ZnO, before using it in the experiment with the Zn electrode. As a result, the CV curve was obtained (Fig. 7).

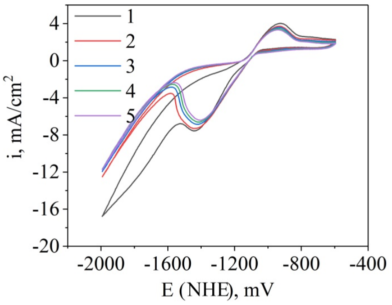


Fig. 7. Cyclic voltammetry curve of the Zn electrode recorded at 10 mV/s in the electrolyte saturated with zincate

As can be seen from the curve (Fig. 7), the zinc electrode can be cycled in the prepared electrolyte. The shape of the CV curve is stable and almost constant from cycle to cycle. However, the peak current densities decrease. The increase in the cathodic current density on the left is related to hydrogen evolution at the tested electrode. Peak current densities have values from 3.3 to −6.3 mA/cm^2 on the fifth cycle, with the tendency of decreasing values. These values are comparable to those obtained from cycling of the silver electrode. However, because the silver electrode has two anodic and cathodic peaks, this electrode has an advantage in capacitive characteristics compared to the zinc electrode.

In [21], it is described that in the potentiodynamic regime at 1 mV/s, the electrochromic electrode based on $Ni(OH)_2$ has a specific capacity of about 0.011–0.0088 mA·h/cm^2. The mesh electrode needs to have such capacity at a small size (minimum wire diameter, large cell size). In the previous part, the silver electrode was chosen as the most promising in the series. However, the cost of silver is rather high [30] and is about 0.5 US $/g. Calculations for the silver electrode showed that only the thin layer of silver, less than 0.5 µm, partakes in reactions. Thus, to save valuable material, it should be possible to use a thin silver coat instead. Therefore, a copper wire coated with a thin layer of silver was used.

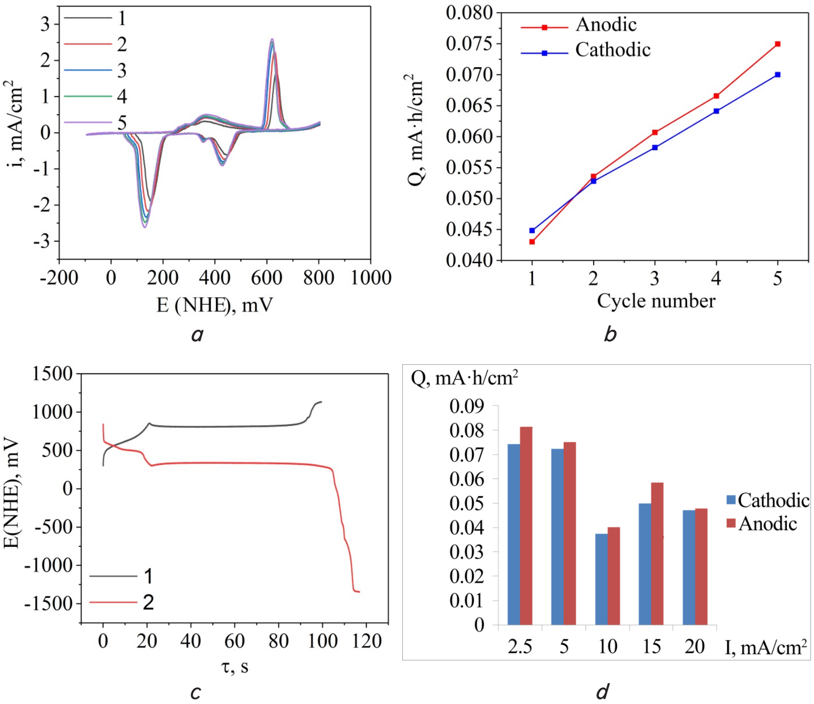
The CV curve was recorded for this electrode to evaluate its capacity. The potential window was narrowed, to limit side reactions that could contribute to the measured capacity, such as electrode decomposition. The scan rate was set the same as for the electrochromic electrode – 1 mV/S (Fig. 8, *a*, *b*) (and not 10 mV/s, as in previous experiments). In addition, specific capacities of silver oxidation and reduction were recorded in galvanostatic regimes at different current densities (Fig. 8, *c*, *d*). The latter was done to evaluate the capacity of the silver electrode in real cycling regimes.

Analysis of the obtained data revealed that for the chosen potential window, only silver partakes in electrochemical reactions – the peaks are similar to the CV curves recorded for the silver electrode recorded previously. Thus, the strategy for saving expensive material does work. In addition, the specific capacities calculated from the CV curves increased with each cycle, reaching 0.07–0.075 mA·h/cm^2 for the fifth cycle. So, the surface area of the silver electrode that would match 1 cm^2 of the electrochromic electrode is equal to 0.011/0.075=0.147 cm^2. If we take the square silver electrode, then one side of it would be equal to the square root of 0.147 cm^2, i.e. 3.8 mm. In case of round wire, the surface that would interfere with light would be even smaller. For instance, for the square mesh with a cell size of 2×2 cm, the diameter of the round wire would be equal to 0.4–0.5 mm. It should be noted that the obtained diameter was calculated assuming one and a half-two time excess of the capacity of electrochromic electrodes.

Analysis of characteristics obtained from galvanostatic cycling revealed that there are two well-distinguished plateaux that correspond to $Ag \leftrightarrow Ag_2O$ and $Ag_2O \leftrightarrow AgO$ transitions. The switch to the third plateau (+1200 and –1200 mV) occurs when the capacity of the electrodes is depleted and electrolyte decomposition starts (Fig. 8, *c*).

The dependency of specific capacities on current density during galvanostatic tests revealed an interesting dependency. Even though the decrease in specific capacity with increasing current density was expected, when the current density increased from 2.5 to 20 mA/cm^2 (i. e. by 8 times), the specific capacity only decreased by 40 % (Fig. 8, *d*). The difference between the anodic and cathodic specific capacities is rather small, indicating high reversibility of the electrode. It should also be noted that maximum specific capacities at minimum current densities are about 0.075–0.082 mA·h/cm^2, which is in agreement with the data obtained from the CV curves.

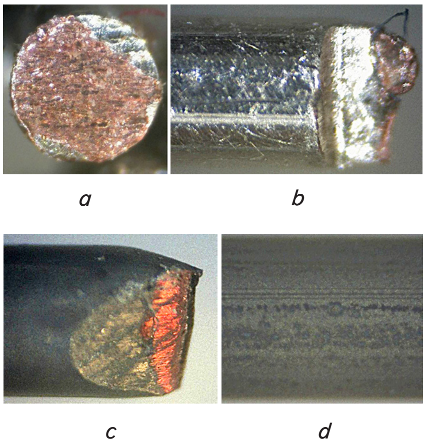
It should also be noted that the silver electrode demonstrated some electrochromic properties and was changing its color from light (initially shiny) to dark, almost black. Fig. 9 shows the initial look of silver-coated copper wire and after cycling.



a *b*

c *d*

Fig. 8. Characteristics of the silver electrode recorded in 0.1 M KOH: *a* – CV curve at 1 mV/s; *b* – specific capacities calculated from CV; *c* – typical characteristics of silver oxidation and reduction during galvanostatic cycling (1 and 2 are oxidation and reduction, respectively); *d* – specific capacities obtained from galvanostatic cycling at different current densities



a *b*

c *d*

Fig. 9. Images of the silver electrode (Ag(Cu) 1.25 mm wire) under an optical microscope at 80x magnification: *a*, *b* – wire before cycling; *c*, *d* – wire after cycling

As can be seen from the presented images, the color of silver changes from shiny to gray-green with dark spots. A pink, uncoated copper can also be observed on the face. Obviously, during electrochemical oxidation Ag transforms into Ag_2O (gray-green in powder), and into AgO (black in powder). Black spots can also be observed in Fig. 9, which correspond to AgO.

6. Discussion of data obtained for studied electrodes

As a result of a rational approach to the design of the electrochromic device, an approach was developed that will lower their cost in future. This approach lies in simplification of the device by replacing part of it with a mesh electrode and using a water-based electrode. Furthermore, based on the known materials used in alkaline batteries and some promising electrochromic materials, a series of possible metal-oxide systems to be used as a mesh electrode were proposed: $Cu|Cu_2O$, Zn|ZnO, Ni|NiO and Ag|AgO.

The CV curves, which were recorded over wide potential windows, revealed the presence of electrochemical activity (Fig. 6).

Unlike others, the zinc electrode did not demonstrate any activity, which is evidenced by the absence of peaks. During cycling of the zinc electrode, only its dissolution was observed, along with gas evolution (Fig. 6, *d*). In this regard, it was decided to saturate the solution with zincate, oxidation of zinc would result in the formation of ZnO (or $Zn(OH)_2$), which would remain on the electrode. Despite that the proposed variant yielded positive results, the zinc electrode had lower specific characteristics than the silver electrode (Fig. 7). In addition, it is unclear how the presence of dissolved zincate would affect the $Ni(OH)_2$ based electrochromic electrode.

The silver electrode proved to be the most promising, as it had the highest specific current densities – up to 5 mA/cm^2 and even higher. Additionally, the CV curve of this electrode showed a constant growth of the peak value with each cycle (Fig. 6. *b*). In turn, the cathode and anodic peaks had about the same, which indicated higher reversibility of the silver electrode. At the same time, the silver electrode had two sets of peaks, which is due two-stage oxidation and reduction of silver. All of this allows to conclude that the silver electrode is more suitable for the proposed design of the electrochromic device, i. e. it is reversible and it would require minimum area.

Some of the chosen systems were experimentally tested for being suitable in the electrochromic device with the mesh electrode. Among the studied systems, only the silver and zinc electrodes showed promise. However, the zinc electrode shows worse performance and requires saturation of the electrolyte with zincate. Therefore, the focus was shifted towards the silver electrode. For cost reduction, it was proposed to use the copper electrode coated with silver.

The obtained characteristics of this material were high and support its usability as a mesh electrode in the electrochromic device (Fig. 8). It was also found that when the current density increased from 2.5 to 20 mA/cm^2 (i. e. by 8 times), the specific capacity only decreased by no more than 40 % (Fig. 8, *d*). The latter allows to speak about the use of this material opens the prospect of creating high-speed electrochromic “smart” windows, they can switch color in tenths of a second. It should also be noted that modern assemblies for large windows require 5 to 10 minutes to switch.

In turn, the zinc electrode could be used after the influence of zincate on the characteristics of the electrochromic electrode was studied.

It should be noted that the use of the silver electrode could be limited due to the low stability of its oxide when exposed to light. This could lead to the electrochromic device with the silver mesh electrode requiring periodic polarization with short impulses to maintain the oxidized state of silver electrode components.

7. Conclusions

1. A new design of the electrochromic device was proposed, which can potentially lower its cost. The design assumes the replacement of the second electrochromic layer along with its conductive layer with a mesh electrode. For the mesh electrode, it is proposed to use a thin copper wire coated with a thin layer of silver. Such design can be used for light and upper parts of view windows. Such type of electrochromic device can be used in cases where full transparency of the device is not required – patient examination rooms, meeting rooms, light control in waveguides.

2. The dependency of specific capacity on current density during galvanostatic cycling of silver was found. It was found that its specific capacity lies within 0.048 to 0.082 mA·h/cm^2.

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