

EFFECT OF LIQUID GLASS COMPOSITION AND STRUCTURE ON THE STRENGTH OF LOW-HYDROGEN ELECTRODE COATINGS

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The paper presents the results of investigations of the strength of coatings of low-hydrogen electrodes, baked at 200, 300 and 400 °C, depending on the composition of liquid Li-, Na- and K-glasses, as well as their binary mixtures. Investigation results were interpreted from the viewpoint of evolution of silicon-oxygen structure of liquid glasses under the conditions of changing kind and ratio of cations-modifiers, as well as the level of water content, related to the parameters of electrode heat treatment. Diagnostics of structural-functional self-organization of silicon-oxygen anions (SOA) in the liquid glass composition was performed with application of the data of nuclear magnetic resonance (NMR). NMR²⁹Si spectrum was used. The generalized results were considered in terms of dominance of polycondensation mechanism. A correlation was established between the values of coating strength and ratio of bridge Q⁴, Q³, Q² and non-bridge Q¹ connectivities in SOA structure. 8 Ref., 4 Tables, 12 Figures.

Keywords: arc welding, welding electrodes, manufacturing technology, liquid glass, liquid glass structure, application of NMR spectroscopy method

Searching for methods to improve the mechanical strength of coatings of low-hydrogen electrodes is an urgent engineering problem:

- violation of the continuity of coatings during their transportation from the manufacturer to the user is the cause for an essential degradation of the quality of electrodes as industrial products;
- spalling and cracks arising in the low-strength coating, cause formation of pores, undercuts and other critical defects in welds, resulting in degradation of their quality and lowering of operational reliability of welded structures;
- low strength of coatings essentially limits the possibilities for improvement of metallurgical characteristics of electrodes, such, in particular, as reaching a low and ultra-low content of hydrogen in the deposited metal, as well as reaching the specified resistance of the coating to absorption of atmospheric moisture. This can be achieved by deep dehydration of the coating, as well as application of liquid glasses, the dry residue of which is non-hygroscopic, that, in its turn is associated with the need to provide its strength.

In view of the above problems, the levels of requirements to coating strength, similar to other quality characteristics of electrode products, cannot be established. Demand practically continuously tightens these requirements. The scientific base underlying development of the respective compositions of electrode

coatings and their manufacture technology, should be also improved, accordingly.

Thus, it is necessary to understand the nature of strength of electrode coatings, clarify the causes for its evolution at the change of material composition and dehydration of liquid glass — the coating binder — at heat treatment of electrodes, as well as find effective techniques, eliminating manifestation of the above drawback.

Electrode heat treatment is usually performed in two stages (Figure 1): low-temperature (air drying or

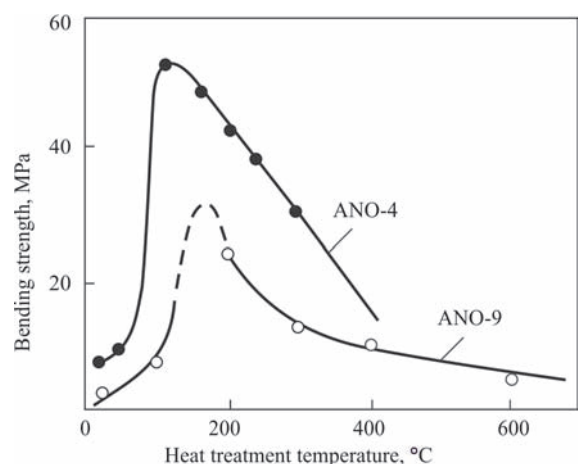


Figure 1. Dependence of strength of cylindrical samples, extruded from covering of electrodes of ANO-4 and ANO-9 grades on heat treatment temperatures [1]

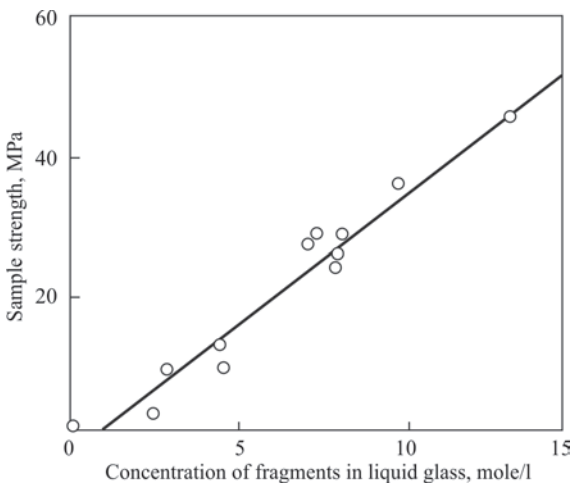


Figure 2. Dependence of strength of silicate stone on total concentration of $\equiv\text{SiO}^- + \equiv\text{SiOH}$ fragments in liquid glass (filler is quartz flour) [2]

heating of electrodes up to the temperature of 140–160 °C) and high-temperature (heating and soaking at 200 °C for rutile and at 400 °C for low-hydrogen electrodes). At the first stage of the process, the coating acquires the specified strength and water resistance. The second stage is introduced with the purpose of achievement of the degree of dehydration, which is required to lower the hydrogen content in the deposited metal. However, coating strength at this stage is reduced considerably.

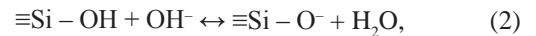
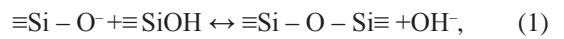
This can be due to dehydration of hydrated forms of silicon-oxygen anions (SOA) in the composition of liquid glass binder, the structure of which determines their binding properties.

The essence of the processes of strength formation proceeding in the coating during the low-temperature stage, can be presented in the case of liquid glass cements — binding compositions of alkaline activation, the hardness of which is determined by molecular distribution of liquid glass components [2]. Formation of silicon-oxygen frame, binding the filler particles into a strong «silicate stone», occurs due to connection of

polymer fragments of different dimensions. At dehydration, it is necessary to take into account water, both that initially introduced into the system as a solvent, and appearing at structure formation due to intermolecular and interfragment condensation.

Additives in the form of calcium silicate powders are used in classic liquid-glass cements to increase the degree of structuring [3]. Hardening of electrode coverings is promoted by marble powder — coating ingredient, which interacts with liquid glass through the reactions of ion exchange and substitution [4].

At application of glass with module $M < 2.5$, in the structure of which Q^1 connectivities prevail, the process of «silicate stone» formation is presented by reactions of condensation of fragments, containing $\equiv\text{SiO}^-$ and $\equiv\text{SiOH}$ groups:



the equilibrium of which is shifted in the direction opposite to dissolution of the silicate block. Strength acquired by «silicate stone» during running of reactions (1) and (2) is proportional to total content of reaction-capable $\equiv\text{SiO}^-$ and $\equiv\text{SiOH}$ groups (Figure 2).

In liquid glasses with silicate module $2.5 < M < 3.0$ reaction-capable silicon-oxygen derivatives with Q^2 and Q^3 connectivities prevail. They have one or two non-bridge bonds. Reactivity of the above SOA groups, moderate in terms of the level, complexity and degree of increase of the stone strength, is compensated by their concentration.

Liquid glasses with $M > 3.0$, containing predominantly Q^4 connectivities, have weak binding properties, and they are not used in liquid-glass cements for these purposes. Degradation of binding capacity of alkaline hydrogel under the influence of Q^4 connectivity should be regarded as the cause for lowering of the coating strength during the second stage of electrode heat treatment, when accumulation of the respective derivatives takes place.

SOA polycondensation is accompanied by a deeper degradation of the matrix structure and lowering of binding capacity of alkaline hydrogel. Concentration of SOA with Q^4 connectivity in the structure can reach critical values and can cause a sharp decrease in coating strength.

The negative, from this viewpoint, degradation of SOA structure with accumulation of Q^4 connectivity in it, was experimentally confirmed.

Figure 3 gives the obtained by IR-spectroscopy method data on the fractions of rigid ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) and elastic ($\equiv\text{Si}-\text{O}^-$) forms of connectivities in the structure of SOA, precipitated from liquid glass of sodium hydrosilicates $\text{Na}_2\text{O} \cdot 2.33\text{SiO}_2 \cdot 6\text{H}_2\text{O}$, depending on dehy-

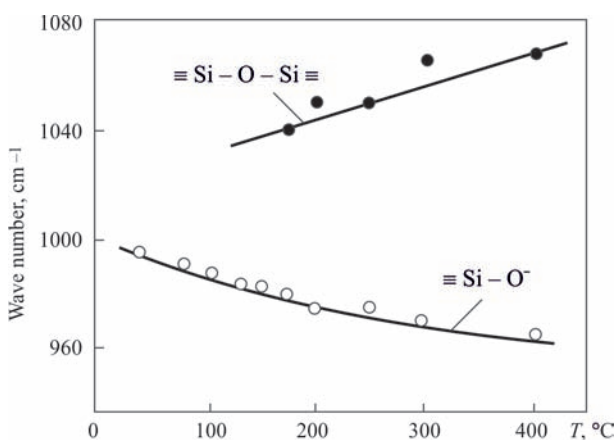


Figure 3. Effect of temperature of sodium hydrosilicate $\text{Na}_2\text{O} \cdot 2.33\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ on SOA structure [5]

Table 1. Chemical composition, density and viscosity of liquid Li-, Na- and K-glasses [6]

Glass type	Module	Weight fraction, %				Steel properties	
		SiO ₂	Li ₂ O	Na ₂ O	K ₂ O	ρ , kg·m ⁻³	η , mPa·s
Li	2.77	25.52	4.60	–	–	1313	325
Na	3.09	28.54	–	8.40	1.70	1433	325
K	3.67	26.37	–	1.66	8.93	1422	360

dration temperature. One can see that increase of dehydration temperature is indeed accompanied by SOA polymerization that results in enrichment of their structure by rigid and brittle elements due to reduction of the fraction of elements with elastic bonds in it.

Object and procedure of investigations. Coatings of test low-hydrogen electrodes, based on mono-alkaline (Li, Na, K) and binary (Li, Na-, Li, K- and Na, K-) liquid glasses with different ratio of alkaline components were selected for study. Binary mixtures were prepared by applying mono-alkaline liquid glasses (Table 1). Lithium glasses were synthesized by wet method, and sodium and potassium ones — by autoclave dissolution of silicate lumps of commercial quality.

Material composition, density ρ , viscosity η , preparation methods, as well as the results of studying the features of binary glass structure with application of NMR-spectroscopy on ²⁹Si nuclei are described in [6].

Structure of liquid glasses was presented as a combination of the fraction of (Q⁴, Q³, Q² and Q¹) connectivities of different complexity in SOA chains and frame, which was determined by the values of integral intensities of signals of ²⁹Si atom nuclei with characteristic values of chemical shifts, measured at room temperature in the spectrometer of AVANSE 400 model of BRUKER Company, Germany [6].

As one can see (Table 1), mono-alkaline Li-, Na-, and K- liquid glasses were used to prepare the coverings, designed for assessment of coating strength, with the same consistency as in [6].

Unlike them, binary glasses were preliminarily brought to the level of viscosity of initial mono-alkaline glasses, by dilution by small water additives, with the aim of leveling the synergetic effect. In liquid Li, K-glasses, containing from 16.3 up to 50.0 wt.% of potassium component, the synergetic viscosity surge reached 20800 mPa·s in the initial condition. Therefore, the degree of their dilution is much greater than that of the other glasses.

Covering with 24 % fraction of liquid glass was prepared in the intensive mixer. Capillary plastometer OB 1435 was used to form from the covering the samples of a cylindrical shape of 4 mm diameter and 40–50 mm length, designed for strength assessment. The consistency of the absolute majority of the coverings allowed producing extrudate of the required quality.

Cracks were found in extrudate billets from four Li, Na-coverings and two Li, K-coverings, differing by a more rigid consistency. In this case, extrudate samples for strength testing were taken from sections not affected by cracks.

After drying in air for one day the cylindrical samples were soaked in the furnace at $T = 150$ °C, and then were baked for one hour stage-by-stage at the temperature of 200, 300 and 400 °C.

Strength of samples was evaluated after cooling to room temperature by the method of three-point bending with application of spring autoplastometer OB 2059. Its standard indenter with conical profile was replaced by a wedge-shaped die for the duration of the tests. The block-diagram of the device for the above tests is presented in Figure 4.

Testing samples of exactly the described configuration allowed observing the change of strength during dehydration of coating material in the pure form without superposition of contributions from thermosetting, thermoelastic (coefficient) and thermal (gradient) stresses, usually arising in coatings deposited on the rods [7].

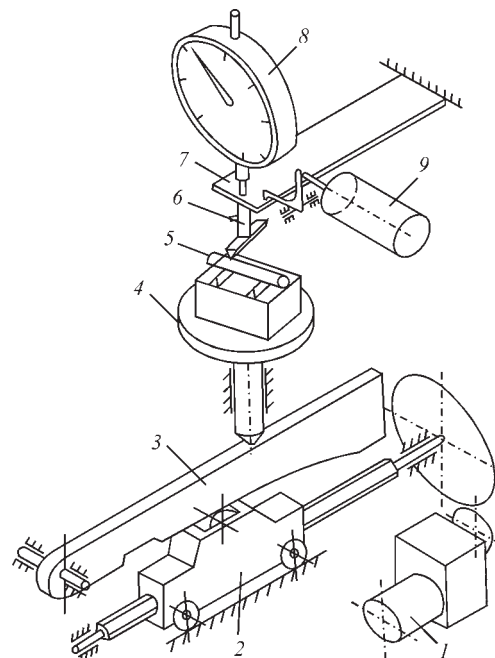


Figure 4. Block diagram of the device based on autoplastometer OB 2059, for determination of strength of ECM samples: 1 — electric drive; 2 — carriage; 3 — guide block; 4 — worktable; 5 — sample; 6 — wedge indenter; 7 — dynamometer; 8 — clock-type indicator of displacement; 9 — self-recorder

Table 2. Characteristics of the structure of SOA in mono-alkaline liquid glasses and strength of ECM samples prepared from them

Kind of glass	Viscosity, mPa·s	Fraction of connectivities in liquid glass structure, %				ECM strength*, MPa at baking temperature, °C		
		Q ¹	Q ²	Q ³	Q ⁴	200	300	400
Li ₂ O·2.77SiO ₂	325	11.2	24.0	38.3	26.5	31.5	21.0	20.5
Na ₂ O·3.09SiO ₂	325	13.0	32.9	38.1	16.0	60.0	47.5	37.0
K ₂ O·3.67SiO ₂	360	10.1	34.7	41.7	13.5	50.0	47.0	44.0

* — average values from five results.

Strength of samples, made with liquid Li-, Na- and K-glasses. Table 2 gives the structural characteristics of mono-alkaline liquid glasses, Qⁿ, and strength characteristics of samples of electrode coating material (ECM) made on their base.

From the data of Table 2 it follows that ECM strength level during dehydration is determined both by chemical composition of liquid glasses, and degree of moisture removal achieved during electrode heat treatment.

Higher strength of samples on sodium silicate base than that of its lithium analogs, is attributable, primarily, to a smaller fraction of rigid connectivities Q⁴ and at the same time greater fraction of elastic connectivities Q² in the glass (content of Q³ structural elements in liquid glasses, which are the base of the compared ECM samples, is the same).

At transition from ECM Na-liquid glass matrix to K-matrix the fraction of bridge connectivities Q⁴ decreases in it and that of elastic Q² and Q³ increases equivalently. Nonetheless, in terms of coating strength, such a replacement turned out to be beneficial only at increase of sample baking temperature up to 400 °C.

The observed effect is certainly related to that the hydroxyl groups are preserved in potassium glass SOA structure up to a higher temperature than that in Li- and Na-glasses [8]. Accordingly, resynthesis of silanol fragments, which are usually broken up by reaction-capable hydroxide ions during dissolution of the silicate lump in an aqueous media, is usually delayed.

NMRS method visualizes the final patterns of the ratio of connectivities in SOA structure under the combined impact of hydroxyl ions and cations-modifiers of hydrosilicate. With increase of electrode baking temperature, the embrittling role of resynthesized structures in lowering of coating strength can become a decisive one.

Influence of combined glasses on ECM strength. Results of determination of the strength of samples of ECM based on binary liquid glasses are given in Figure 5.

As one can see the interconnection between the composition of binary alkaline hydrosilicates in the

space between the coating ingredient grains and depth of their dehydroxylation during electrode heat treatment and ECM strength is ambiguous.

This applies both to the nature and degree of the above influence.

1. Substitution of Li-cations-modifiers having a higher energy potential, compared to Na⁺ or K⁺ (they are characterized by smaller Z/r values) in the composition of liquid Li, Na- and Li, K-glasses, is accompanied by a considerable increase of the strength of ECM samples in the entire range of baking temperatures (dotted lines). The higher the baking temperature, the lower the total level and degree of increase of sample strength. At the same time, the nature of change of the strength of ECM samples, based on liquid Na, K-glasses with different ratio of Na- and K-components in the mixtures, depends on the conditions of sample heat treatment. So, the strength of samples, baked at 200 °C, decreases, and that of samples baked at 300 °C, remains at an approximately constant level. However, in the case of samples baked at 400 °C, it increases at increase of the fraction of K-component in the mixture.

2. In the range between the extreme values, the sample strength changes non-monotonically, depending on the fraction of the substitution component in binary binder. It deviates from the additive value, both to the lesser (in the left part of the diagram) and to the greater (in the right part of the diagram) level.

Minimums of strength are expressed to the greatest extent in Li, K-compositions, their depth somewhat decreasing with increase of the degree of sample dehydration, resulting from increase of their baking temperature.

The observed initial minimal values of strength are expressed to the smallest degree in Li, Na-compositions. In Na,K compositions the left, weak minimum of strength, is observed in samples, dehydrated at 300 °C; with increase of the degree of dehydration the depth of the minimum somewhat increases.

3. Degree of singularity of maximums of strength values in the right part of the diagrams also depends on the combination of the applied liquid glasses and temperature of ECM sample heat treatment. In Na,

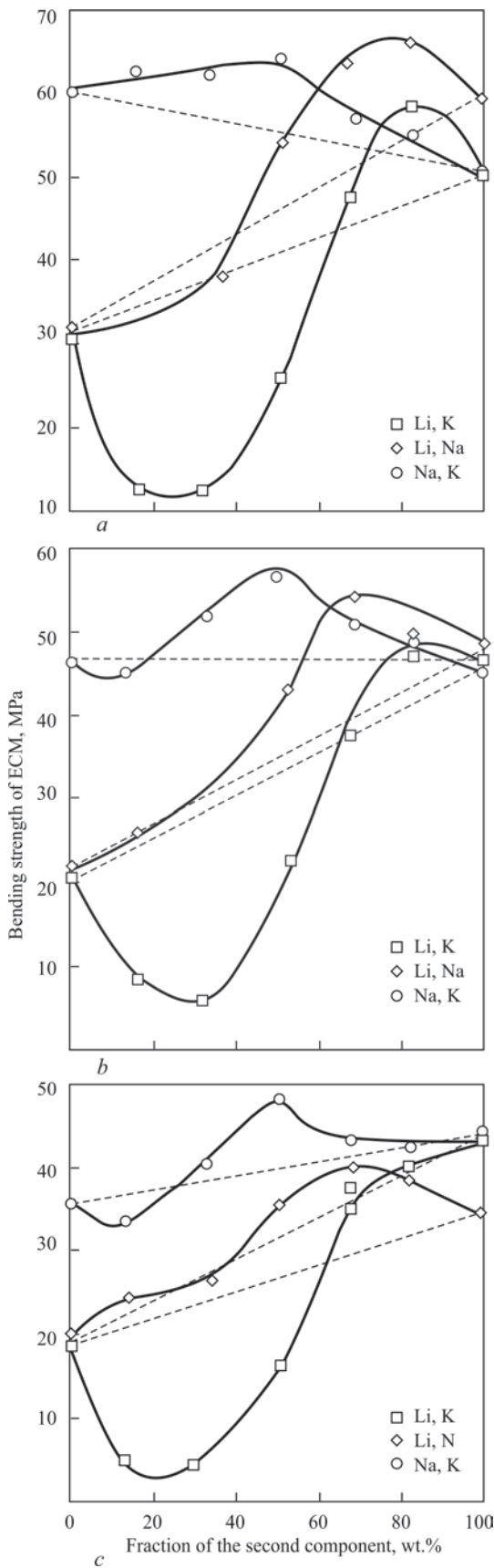


Figure 5. Influence of the composition of binary liquid Li, Na-, Li, K- and Na, K-glasses on the strength of ECM samples, baked at 200 (a), 300 (b) and 400 °C (c)

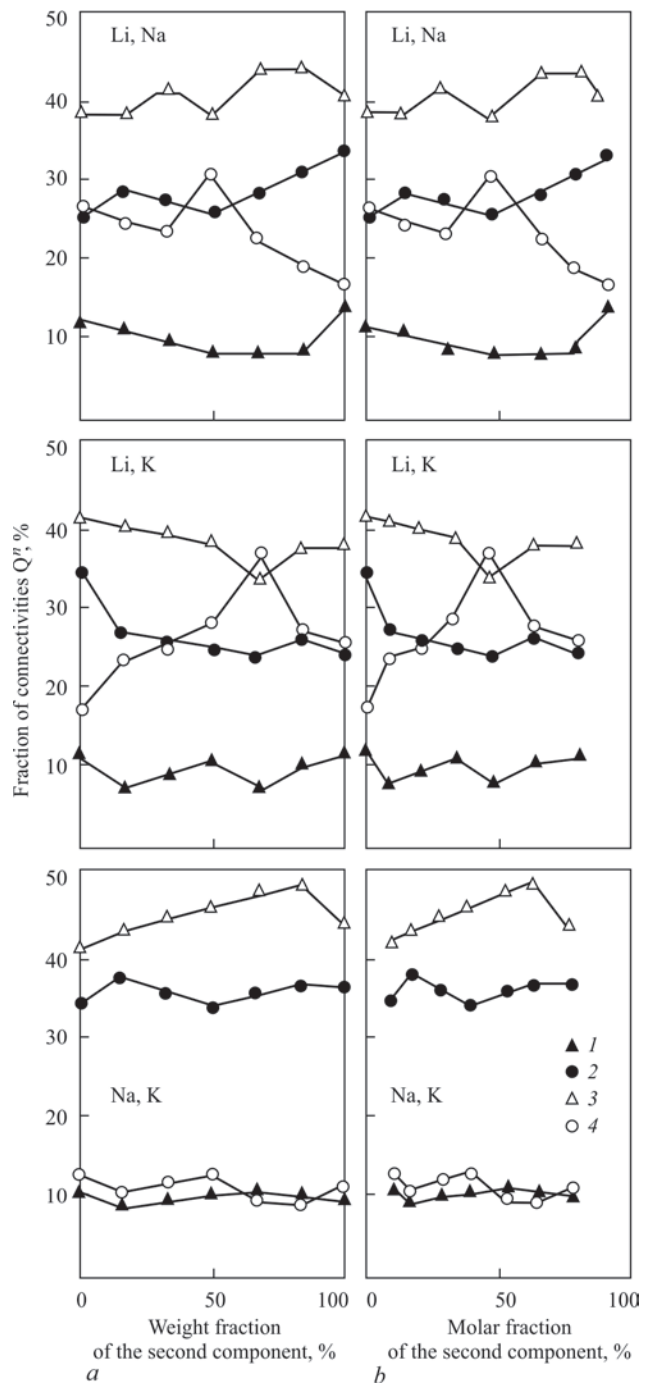


Figure 6. Evolution of NMR²⁹Si parameters of combined liquid Li,Na-, Li,K- and Na,K-glasses, depending on weight (a) and molar (b) ratio of mono-alkaline components included into them (1 — Q¹; 2 — Q²; 3 — Q³; 4 — Q⁴)

K-series of samples the strength values in the maximum rise with T_b increase, in Li, Na they decrease and are blurred, and in Li,K they completely degenerate.

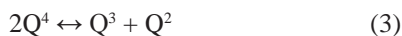
The above configuration features of strength diagrams of electrode compositions based on binary liquid glasses, can be attributed to availability of a wide range of structural forms of silicates, which are formed in the final silicon-oxygen matrix and determine the composition strength, as well as the complexity and diversity of the processes, i.e. presence

of several directions of mutual transformation of the above forms.

Features of structural-functional transformations, due to variation of the composition of binary liquid glasses. Using the NMR²⁹Si spectroscopy data given in a generalized form in Figure 6, we will consider, first of all, how the ratio of structural forms of silicates in binary liquid Li, Na-, Li, K- and Na, K-glasses changes.

So, in the structure of liquid Li,Na-glasses the fraction of connectivities Q³, compared to other kinds of the considered binary liquid glasses, is maximum, and is on the level of 40 %, irrespective of the ratio of the lithium and sodium components.

Judging by the stoichiometry, the following exchange reactions can run in structural transformations of this group of liquid glasses:



With increase of the fraction of the sodium component in the mixture, the concentration of Q² structural units rises monotonically (from 25 up to 35 %), and Q⁴ decreases from 25 to 18 %, respectively.

For a mixture with equal fractions of Li- and Na-components (mass and molecular) the content of Q⁴ structural units reaches the maximum value, and stoichiometry of equation (3) is fulfilled with maximum accuracy. The same applies to equation (4) for mixtures, containing 16.3 and 83.7 % of sodium component.

In liquid Li,K-glasses at almost constant content of Q¹ (on the level of about 10 %) and Q³ (on the level of 40 %) the fraction of Q² connectivities decreases with the mixture enrichment in potassium component from 35 up to 25 %.

Here, the fraction of Q⁴ connectivities first rises nonmonotonically from 15 up to 25 %, and then goes through a maximum equal to 38 %, at 68 % weight fraction of K₂O in the mixture.

In some NMR²⁹Si spectra of this group of liquid glass samples, indications of stoichiometric running, according to equations (3)–(5), of exchange reactions between SOA structural elements, were also revealed.

So, it follows from Figure 6 that, similar to the previous series of experiments, the maximum fraction of Q⁴ structural units was registered in the mixtures of glasses with molar ratio K₂O/Li₂O = 50/50. The highest value of weighted average of connectivity Q^m corresponds to it. Interactions according to equations (3)–(5), for mixtures with the second component fraction of 50.0; 83.7; and 66.7 wt.%, respectively, turned out to be close to stoichiometricity.



Alongside that it was found that exchange reactions with participation of lower forms of connectivity Q¹ and Q², proceed in the composition of lithium glass and in the majority of the studied binary mixtures with sodium and potassium components. These reactions can be presented by equation (6).

Constant (on the level of 10 and 12 %) Q¹ and Q⁴ contents are registered in liquid Na, K-glasses, and Q² and Q³ connectivities have a decisive influence on their properties. The fraction of the first of them does not depend on the mixture composition, and remains on the level of about 35 %, and the fraction of the second one rises linearly from 40 up to 48 % with increase of the content of potassium component in the mixture. Then it drops to the level characteristic for the initial potassium component.

The degree of correspondence to the stoichiometricity on the level of 80 % was revealed for interactions, which are described by equations (4) and (6).

Comparing the data of Figures 5 and 6, it can be assumed that the highest level of strength of dehydrated coverings, based on liquid Na, K-glasses, is associated with the low total fraction of Q⁴ connectivities. The total fraction of Q² + Q³ connectivities is weakly dependent on K₂O/Na₂O ratio in the glass mixture. Accordingly, strength of the coating, which is determined by (Q² + Q³) characteristic, also changes only slightly. In Figure 5, the dotted line marks the overall tendency of σ_{ch} change, under the influence of the second component in the mixture: it decreases (T_b = 200 °C), remains unchanged (300 °C) or increases (400 °C) with T_b increase, and is determined, most probably, by the features of dehydration of hydrosilicate matrix in the presence of the potassium component.

The level of strength of the coverings, based on liquid Li, Na-glasses, is lower than that in the previous series, as a result of the lower total fraction of (Q² + Q³) connectivities in liquid glass. Relatively more significant increase in strength is attributable to greater total fraction of (Q² + Q³) connectivities due to equivalent reduction of the fraction of Q⁴-type connectivities in liquid glass.

The lowest strength values of dehydrated coverings are observed in the series of experiments with Li, K-glasses, particularly those based on mixtures with a low content of the second component.

Features of molecular-weight distribution of SOA elements. Let us consider the interrelation between the weighted average value $Q^m = \sum x_i Q_i^n$ and molecular-weight distribution of SOA elements in the studied alkaline-silicate systems, where Qⁿ_i is the cur-

rent value of Q^n , and x_i is their fraction in the total number of connectivities.

It follows from Figure 7 that the strength of ECM samples is inversely proportional to the negative value of structural characteristic Q^m . Strength values are stratified into 4 groups, shifted relative to each other along the abscissa axis. The first, the largest group, designated by index 1, is mostly represented by samples of Li, Na-, Li, K- and Na, K-series. The other form a small group II, as well as isolated III and IV groups. Assessment of the material and molecular-weight compositions of liquid glasses, as well as the value of strength of dehydrated coverings based on them, is given in Table 3.

Maximum value of strength (50 MPa) was achieved on the sample of Na,K-16 coating in group II. It is stated above that this sample is based on liquid glass with 50 wt.% of the potassium component. Its structure is presented as follows: 10 % contribution of Q^4 connectivities, and the fraction of Q^3 and Q^2 connectivities reaches 45 and 35 %, respectively. Deviation of the ratio of alkaline components from the optimum value only slightly affects the strength of coatings of this group, and has little effect on the ratio of structural formations in the composition of liquid glass SOA. The value of coating strength rarely drops below 35 MPa.

Minimum values of strength (2.5–5.0 MPa) were found in Li, K-12 and Li, K-13 samples from group I, based on liquid Li, K-glasses, in the composition of which the fraction of the potassium component changes in the range of 10–25 % of the mixture. In the structural distribution of SOA of these glasses Q^3 connectivities account for 40 %, and Q^2 and Q^4 con-

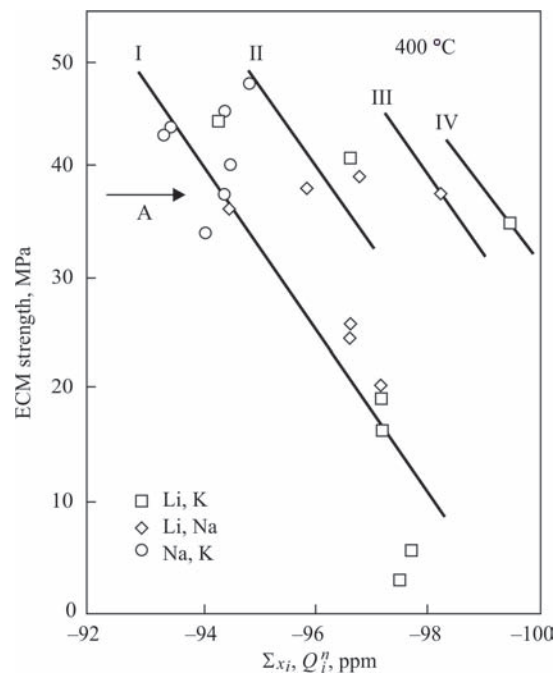


Figure 7. Interrelation of strength of ECM samples made from binary liquid Li, Na-, Li, K- and Na, K-glasses and weighted average values of connectivities in SOA structure (for designations see the text)

nectivities are equal to 25 % each. This result is notable for the following reasons:

- above-mentioned strength is 4–8 times lower than that of samples based on the mono-alkaline lithium liquid glass;
- fraction of Q^4 connectivities in SOA structure is almost the same, as in the case of the lithium glass (about 25 %). The largest total fraction of connectivities ($Q^3 + Q^4 \approx 65 %$), was revealed in the composition of exactly those binary liquid Li, K-glasses, which provide the lowest coating strength;

Table 3. Interrelation of strength of ECM samples with structural characteristics of SOA of binary liquid glasses (I–IV groups)

Test index	Test group	Liquid glass composition	Fraction of connectivities, %				Q^m , ppm	σ , MPa
			Q^1	Q^2	Q^3	Q^4		
Na, K-15	I	$0.48Na_2O \cdot 0.52K_2O \cdot 3.40SiO_2$	10.3	34.4	47.0	9.0	93.5	42.8
Na		$0.88Na_2O \cdot 0.12K_2O \cdot 3.10SiO_2$	13.1	32.9	38.1	16.0	94.5	36.9
Li, Na-8		$0.85Na_2O \cdot 0.52Li_2O \cdot 2.83SiO_2$	11.0	27.8	37.8	23.4	96.7	23.8
Li		$Li_2O \cdot 2.77SiO_2$	11.2	24.0	38.3	26.5	97.3	20.4
Li, K-11		$0.65Li_2O \cdot 0.35K_2O \cdot 3.13SiO_2$	10.6	24.1	38.4	26.9	97.3	16.3
Li, K-13		$0.89Li_2O \cdot 0.11K_2O \cdot 2.90SiO_2$	7.0	25.1	40.5	27.3	97.9	4.6
Li, K-12		$0.78Li_2O \cdot 0.22K_2O \cdot 3.00SiO_2$	8.5	25.1	40.0	26.4	97.6	2.9
Na, K-16	II	$0.59Na_2O \cdot 0.41K_2O \cdot 3.31SiO_2$	9.6	32.4	45.3	12.6	94.7	49.8
Li, Na-5		$0.36Li_2O \cdot 0.64Na_2O \cdot 3.00SiO_2$	7.5	27.2	43.3	22.0	97.0	39.2
Li, K-9		$0.37Li_2O \cdot 0.53K_2O \cdot 3.42SiO_2$	10.5	26.7	37.8	25.0	96.8	41.3
Li, Na-6		$0.53Li_2O \cdot 0.47Na_2O \cdot 2.94SiO_2$	7.2	25.1	36.9	30.8	98.3	37.0
Li, Na-5	III	$0.36Li_2O \cdot 0.64Na_2O \cdot 3.00SiO_2$	7.5	27.2	43.3	22.0	98.0	39.6
Li, K-10	IV	$0.52Li_2O \cdot 0.48K_2O \cdot 3.27SiO_2$	6.6	23.5	33.0	36.9	99.5	35.5

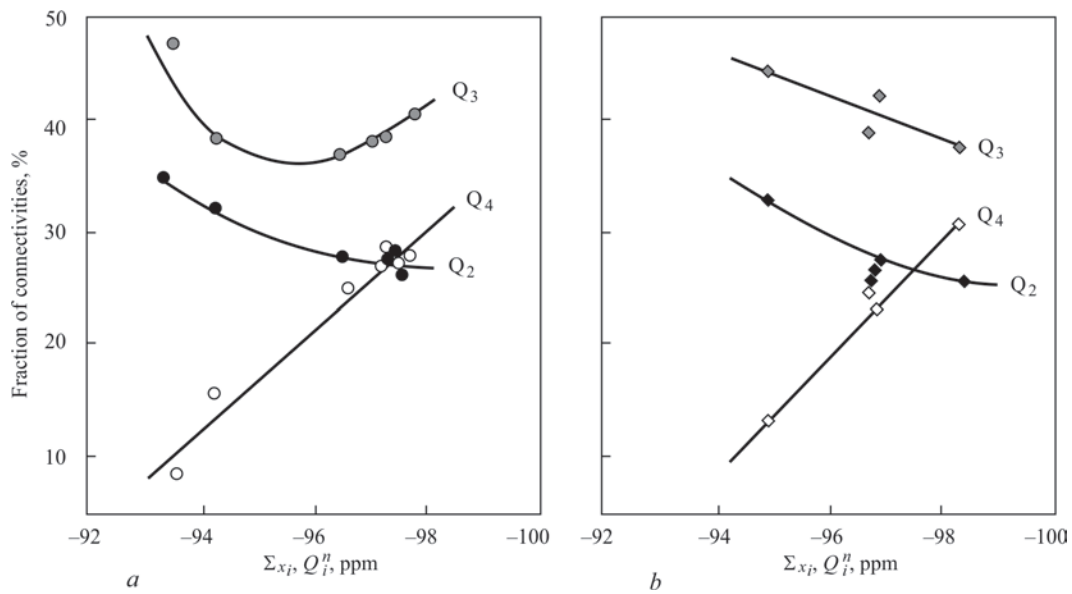


Figure 8. Distribution of chemical shifts Q^n in liquid glasses, used for producing coatings in test groups designated by indexes I (a) and II (b) (see Table 3)

• fraction of Q^4 connectivities in SOA structure reaches 30 and 37 %, respectively, in the structure of some combinations of lithium glass with potassium and sodium liquid glasses (for instance, Li, Na-6 and Li, K-10 experiments). Here, the total fraction of connectivities ($Q^3 + Q^4$) reaches 65–70 %. In mono-alkaline liquid glasses such a significant prevalence of spatially-diverse structural connectivities over the non-bridge ones, does not occur at all [2]. Therefore, their formation is the result of simultaneous multisite interaction of binary mixture components. Despite that, the strength of the above-mentioned ECM samples does not drop below the values of 35 MPa.

Thus, increase of the fraction of complex forms of connectivities should be regarded as the main cause behind lowering of coating strength (in group I it rises three times, reaching the value of 27 %, in series II — 2.5 times, reaching the value of 30.8 %). This is due to reduction of the total fraction of connectivities ($Q^2 + Q^3$). As follows from Figure 8, this transformation of SOA structures proceeds differently in the compared groups.

In group I, in which the initial Q^m value is lower, and the fraction of bridge connectivities is higher, than in group II, increase of Q^4 contribution occurs due

to lowering of the total content of ($Q^2 + Q^3$) groups. However, at Q^m with $\delta < -96$ ppm, the change of Q^2 fraction becomes smoother, and lowering of Q^3 content is replaced by its significant increase, resulting in the total fraction of connectivities ($Q^3 + Q^4$) reaching 70 %. This, most probably, is what provokes the catastrophic drop of the strength of samples of Li,K-series with 11, 12 and 13 indices.

Structure of liquid glasses in samples of group II changes more smoothly. The overall increase of the number of Q^4 connectivities is completely compensated by total decrease of the fraction of more elastic kinds Q^2 and Q^3 .

Synchronous change of the ratio of connectivities occurs at formation of the structure of Li, Na-5 and Li, K-10 samples (see Table 3).

Another variant of interrelation of SOA structure with ECM strength was revealed: similar to test series designated by II–IV indices, degradation of hydrosilicate binder due to increase of Q^4 connectivities is damped by the change of the quantity of Q^2 and Q^3 connectivities (Table 4; Figure 9).

Here, the fraction of elastic Q^2 connectivities decreases continuously, and that of the less elastic one Q^3 is reduced after it has reached, in the sum with

Table 4. Strength of ECM samples of group A

Test index	Liquid glass composition	Fraction of connectivities, %				Q^m , ppm	σ , MPa
		Q^1	Q^2	Q^3	Q^4		
Na	0.88Na ₂ O·0.12K ₂ O·3.10SiO ₂	13.1	32.9	38.1	16.0	94.5	36.9
Li, Na-4	0.19Li ₂ O·0.81Na ₂ O·3.05SiO ₂	7.9	30.3	43.4	18.4	96.1	38.7
Li, Na-5	0.36Li ₂ O·0.64Na ₂ O·3.00SiO ₂	7.5	27.2	43.3	22.0	97.0	39.2
Li, Na-6	0.53Li ₂ O·0.47Na ₂ O·2.94SiO ₂	7.2	25.1	36.9	30.8	98.3	37.0
Li, K-10	0.52Li ₂ O·0.48K ₂ O·3.27SiO ₂	6.6	23.5	33.0	36.9	99.5	35.5

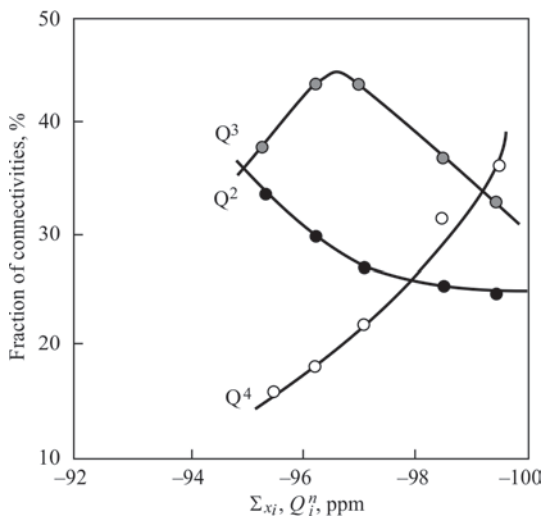


Figure 9. Distribution of connectivities Q_i^n in liquid glasses of test group designated by A index (see Table 4)

Q^4 connectivity, a critical value in terms of coating strength.

The interrelation between material composition, degree of dehydroxylation of alkaline-silicate binder and SOA molecular-weight distribution, as well as coating strength. Mechanical strength of electrode coating forms under the conditions of joint action of cations-modifiers and hydroxide-ions in the liquid glass composition on SOA structure. Cation ratio is determined by liquid glass composition. It can improve or degrade the SOA structure in the liquid glass, and, therefore, increase or decrease the coating strength. Hydroxide-ion concentration is determined by the degree of SOA dehydration at electrode heat treatment. Alongside temperature, it is also influenced by SOA water retention capacity, which, in its turn, depends on their structure, determined by the ratio of cations-modifiers in their composition. At baking temperatures, characteristic for manufacturing low-hydrogen electrodes, degradation of coating strength usually prevails.

The cumulative effect of cations-modifiers present in the composition of alkaline hydrosilicates, on the one hand, and degree of their dehydroxylation at electrode baking, on the other hand, on SOA structure and coating strength, can be separated, by applying instead of the moisture content of the coating, which was not yet studied in this work, its «Siverts equivalent» in the form of hydrogen content in the deposited metal.

Figure 10 gives the results of comparison of the content of diffusible hydrogen in the metal, deposited with electrodes based on liquid Na, K-, Li, Na- and Li, K-glasses.

One can see from the data of Figure 10 that hydrogen content in the deposited metal changes in the ranges from 5.7 up to 7.7 ml/100 g of deposited met-

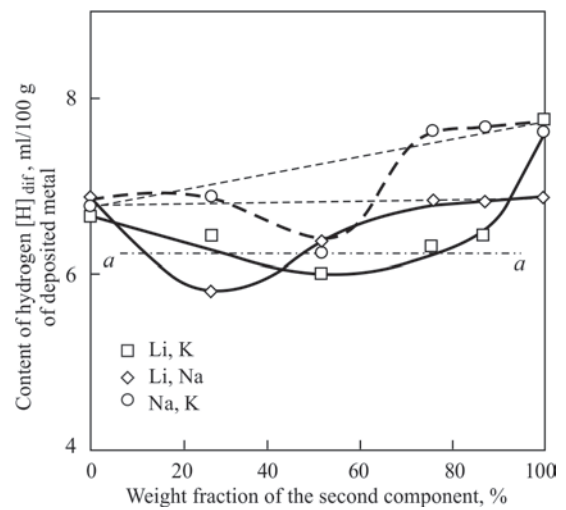


Figure 10. Comparison of hydrogen content in the metal deposited with electrodes based on liquid Li, Na-, Li, K- and Na, K-glasses (electrode baking temperature of 400 °C)

al, depending on the composition of the studied liquid-glass binders of electrode coating. The observed lowering (in the minimum) is similar for all the series of glasses, whereas the position and extent of the extremum along the concentration axis changes significantly for all the samples at transition from series to series, and the curves representing the change of hydrogen content in the deposited metal, intersect in the point corresponding to equal weight fractions of the components of binary mixtures. For Li, Na-series of samples the point of intersection of the curves becomes close to, and for Na, K and Li, K-series it exactly corresponds to $[H]$ minimum, recalculated to deposited metal.

As follows from Figure 7, the strength of ECM samples based on liquid Na, K-16, Li, Na-6 and Li, K-11 glasses changes from 16 to 50 MPa, i.e. 3 times. Considering the same content of hydrogen in the de-

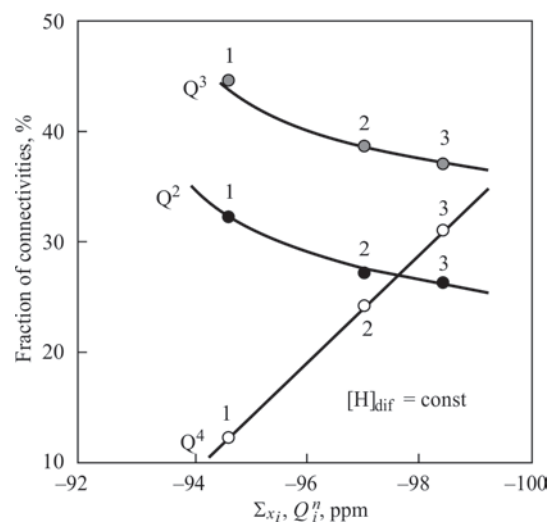


Figure 11. Distribution of connectivities Q_i^n in liquid glasses, used for producing ECM with indexes Na, K-16 (1), Li, Na-6 (2) and Li, K-11 (3)

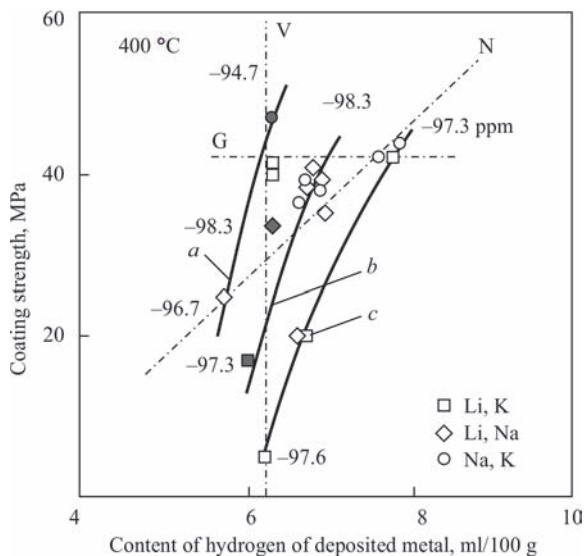


Figure 12. Interrelation of strength of low-hydrogen electrode coatings, based on liquid Na, K-, Li, Na- and Li, K-glasses, with hydrogen equivalent of their moisture content; electrode baking temperature of 440 °C (for designations see the text)

posited metal, we can assume that moisture content of initial electrode coatings remains unchanged. Therefore, three times change of ECM strength is due to the dynamics of structural components of SOA of binder composition under the influence of cations-modifiers. This is confirmed by the data in Figure 11.

The sample of Na,K-16 coating is the most dehydrated. Nonetheless, it is the strongest one in Na, K-series. This is indicative of the fact that lowering of the strength of ECM structure during dehydration of binary binder can be compensated by such a transformation of SOA structure under the impact of the change of the ratio of alkaline modifiers content, which will be favourable for strength formation. For one composition of the binder, the above transformation partially, and for another — completely compensates, and for the third one it even exceeds the lowering of strength, due to dehydration of the alkaline silicate binder.

Figure 12 shows the dependence of the strength of ECM samples based on liquid Na, K-, Li, Na- and Li, K-glasses, on hydrogen content in the deposited metal.

One can see here that the figurative points, expressing σ_{ch} value, were stratified into three layers, designated by indices *a*, *b*, *c*, that are supposedly associated with the change of average weighted value of Q^m , which is caused by degradation of SOA structure: the larger Q^m , the greater the shifting of the respective curve along the abscissa axis. Symbols V, G and N designate the results of experiments located along the straight lines, oriented normal, in parallel and obliquely relative to the abscissa axis.

Results of tests oriented along the vertical, characterize the strength of coating samples with the same moisture level. Therefore, their strength is determined exclusively by the ratio of contributions of connectivities, dependent on SOA chemical composition and structure. They include also the above-considered Na, K-16, Li, Na-6 and Li, K-11 samples, which are designated by shaded points in Figure 12. In their structure the fraction of Q^4 connectivities grows in proportion to decrease of both the angle of inclination of a curve, characterizing the yield of connectivities ($Q^3 + Q^2$), in Figure 11, and ECM strength. The same pattern is found in experiments with the other samples of this group.

In samples located along the horizontal, $\sigma_{ch} = \text{const}$. Therefore, decrease (increase) of strength, determined by increase (decrease) of their moisture level, is completely compensated by the correcting change of SOA structure, associated with the impact of the ratio of cations, determining the formation of strength. Numbers near $\sigma_{ch} = f([H])$ curves express the nature of change of Q^m characteristic.

Dependencies shown by *a*, *b*, *c* and N lines, characterize the resultant of the parameters of the change of SOA structure and σ_{ch} , connected with the dynamics of chemical composition and simultaneous dehydration of liquid glass in the range between V and G values.

Conclusions

1. Strength of electrode coatings, similar to other kinds of filled compositions, which are the objects of silicate technologies, is determined by binding properties of the hydrosilicate matrix. The above parameter depends on the material and structural composition of the liquid glass used as the binder, as well as the degree of its dehydration at electrode heat treatment. Here, the composition of alkaline hydrosilicate matrices of electrode coatings, interrelated with the change of structure and water retention capacity of the hydrosilicate binder, determines the features of formation of the coating strength, while electrode heat treatment leads to degradation of the structure and lowering of the strength of coatings as a result of dehydration.

2. Maximum high level of coating strength is provided by the systems of combined liquid sodium-potassium glasses, in the structure of which the fraction of rigid and brittle silicon-oxygen (bridge) connectivities seldom exceeds 10 %, and the base of the structural matrix (about 80 %) is usually made up by elastic connectivities ($Q^2 + Q^3$).

3. The lowest level of coating strength is observed at application of lithium-potassium glass with 10–40 % content of the potassium component, as a

binder, the effect of which is usually demonstrated by a considerable synergetic surge of viscosity. The strength of coatings based on liquid glasses of such a composition, is even lower than that of coatings based on pure lithium glass.

4. Prospects are opened up for solving the problems, arising in connection with the low strength of coatings based on lithium liquid glasses, through application of combined liquid Li-, Na-, K-glasses.

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