

Germanium Electrode in an Electrochemically Active Heterostructure with Hydroxide Proton Conductor at Room Temperature

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Abstract—A macroscopic heterostructure synthesized in the form of a germanium–hydroxide proton conductor–graphite assembly generates electric voltage comparable with that in polymer microfuel cells (0.7 V). Germanium-containing heterostructures, operating at room temperature and involving no precious metals, can be used as electric current sources for low-power devices. From the fundamental standpoint, a new combination of solid hydroxide proton conductors with group-IV electrodes is also of interest.

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At present, the interest in various electrochemically active structures is determined primarily by the efficiency of their operation in sources of electric current and/or voltage for various technical applications. The search for and development of electrochemical cells with new electrolytes or new electrode–electrolyte assemblies is based on fundamental investigations of the electrochemical activity of materials. Moreover, the main requirement to new cells consists in the compatibility of new electrolytes with well-known electrodes and new electrodes with well-known electrolytes.

This Letter considers a new search direction, the novelty of which is determined by the previously unknown combination of well-known materials in a membrane–electrode assembly. These are a solid electrolyte based on potassium hydroxide monohydrate and a semiconductor electrode material (germanium). We have experimentally studied electrochemically active cells of the $(-)\text{Ge}|\text{KOH} \cdot n\text{H}_2\text{O}|\text{C}(+)$ type.

We have originally studied this electrolyte (KOH monohydrate) since 2007. It is a member of the family of water–potassium hydroxide system that is well and long known in the physical chemistry. Our interest was devoted to $\text{KOH} \cdot n\text{H}_2\text{O}$ hydrates with $n = 0.5, 1.0,$ and 2.0 [1, 2]. Graphite (C), which is well known as a polyfunctional electrode material, was been initially used in our investigations as a counter-electrode for Ni, Ti, TiFe intermetallide, and metallic tin (Sn). Recently, it has been shown [3] that silicon (Si) in heterostructures with solid potassium hydroxide mono- and dihydrate exhibits electrochemical activity, the character of which depends on the doping level. It was naturally of interest to expand the group of previously studied electrode materials (C, Si, and Sn) in contact with solid

hydroxide proton conductors by including another group-IV element—germanium (Ge).

Below, we present the main results of current–voltage ($I-U$) and impedance measurements for a $(-)\text{Ge}|\text{KOH} \cdot x\text{H}_2\text{O}|\text{C}(+)$ type cell with $x = 1.05$. The choice of this electrolyte composition with a crystallization temperature between 130 and 147°C simplifies the technology of cell formation and eliminates undesired premelting effects during room-temperature measurements. The function of electrodes was performed by p -Ge plates ($\rho = 28 \Omega \text{ cm}$) and analytical-grade graphite rods with a diameter of 6 mm. The interelectrode distance was about 1 cm. The room-temperature resistivity of the electrolyte was within 1.3–2 k Ω . The internal volume of a cell was $\sim 7 \text{ cm}^3$ for a tube and 10 cm^3 for a specially designed Teflon cup. In the latter cell, an additional (third) Pt electrode was introduced into the electrolyte in order to measure the electrode potentials relative to this reference electrode.

The cells were assembled in a closed box filled with nitrogen. Preliminarily, a Ge electrode was fixed in the cell in air. Then, the cell was heated in the nitrogen-filled box to $\sim 100^\circ\text{C}$ and filled with electrolyte (melted at 150°C), after which the assembly was completed by introducing the graphite electrode. As a rule, a potential difference of 0.5–0.8 V appeared on the cell in about 5–10 min and was retained during slow cooling (which was necessary for correct formation of the electrolyte volume) down to room temperature. During subsequent storage in a closed volume in the absence of an external load, the potential difference was retained on a level of 0.7 V for a time period of no less than half a year. Moreover, if a cell was used in experiments as a source of current through an external

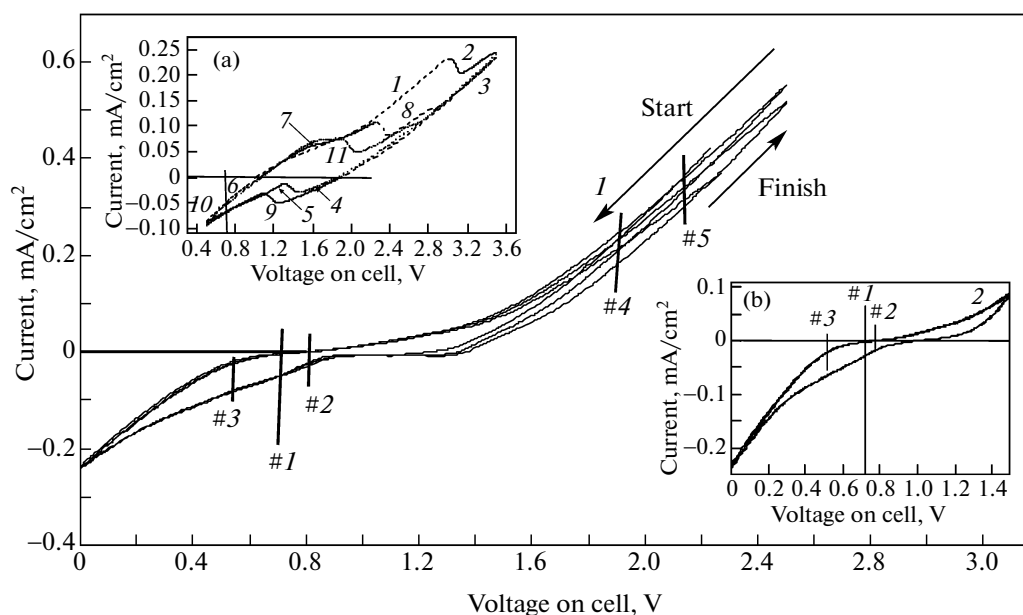


Fig. 1. Current–voltage characteristics of the (+)C|KOH · xH₂O|Ge(–) type cell measured at 295°C in various voltage intervals: (curve 1) 0–2.4 V; (curve 2, inset (b)) 0–1.5 V; (curve in inset (a)) 0.4–3.4 V. Markers 1–5 at curves 1 and 2 correspond to the numbers of impedance curves in Fig. 3. Numbers in inset (a) indicate the order of passage of the corresponding I – U region on cycling.

load or tested in a regime analogous to battery charging, the potential difference on the cell returned to the same level of 0.7–0.72 V. Therefore, it would be natural to consider this value as the room-temperature (295°C) emf of the cell. The temperature dependence of the emf requires special investigation and is beyond the scope of this article. The reported experiments were performed within 23–25°C. The current–voltage and impedance measurements were performed using a Solartron 1260 setup in a frequency range of 1 mHz–2 MHz. The lack of differently doped p -Ge samples did not allow us to gain information on related variations of the thermodynamic parameters of electrochemical activity, which had been previously observed for electrochemically active heterostructures with Si electrodes [3].

Let us consider kinetic aspects of electrochemical activity of the proposed heterostructures. Below we present the results of I – U and impedance measurements for cells in the “as-prepared” state, without any attempts to improve their characteristics, e.g., by special preparation of electrodes and/or variation of the electrolyte composition. To the best of our knowledge, the available literature contains no results of investigation (and even more so application) of heterostructures of the solid alkaline electrolyte–semiconductor type. Therefore, our study is an alternative to numerous investigations of the cells combining semiconductor electrodes with electrolytes possessing acid properties or occurring in the liquid state (see, e.g., [4], where the behavior of Ge was studied in NaOH solutions).

The manufactured cells were stored at room temperature. Owing to a closed structure, the cells were not in contact with the ambient atmosphere and their characteristics (emf, open-circuit impedance, weight) remained unchanged for several weeks. Prior to the main experiments, the cells were “trained” in a regime of cyclic I – U measurements in an interval from 0.4 to 4 V—i.e., on both sides of the equilibrium state of 0.7 V, Ge(–) (see inset (a) to Fig. 1, where numbers indicate the order of passage of the corresponding region on cycling). After five or six cycles (20 mV/s), the I – U curve shape exhibited stabilization and was well reproduced in subsequent measurements even in 2–3 days. It should be noted for the following discussion that, at a cell voltage above 0.7 V, a negative potential on the Ge electrode increases in absolute value, which leads to hydrogen evolution and/or hydrogenation of germanium. This was qualitatively observed in special experiments with monitoring of the gas medium in the space above the Ge electrode. However, the current yield in this regime did not exceed 15%. The greatest amount of current was probably spent for the formation of hydride forms, as has been pointed out in many investigations [5, 6]. These facts and ideas were taken into account in the analysis of cyclic I – U characteristics of the cell under consideration.

Figure 2 reconstructs curves 1 and 2 from Fig. 1 in $\log(|j|)$ – η coordinates, where η is the overvoltage—i.e., deviation of the voltage on cell from that in the equilibrium open-circuit (!) state. For the sake of convenience, the data for curve 2 of Fig. 1 are shown in the

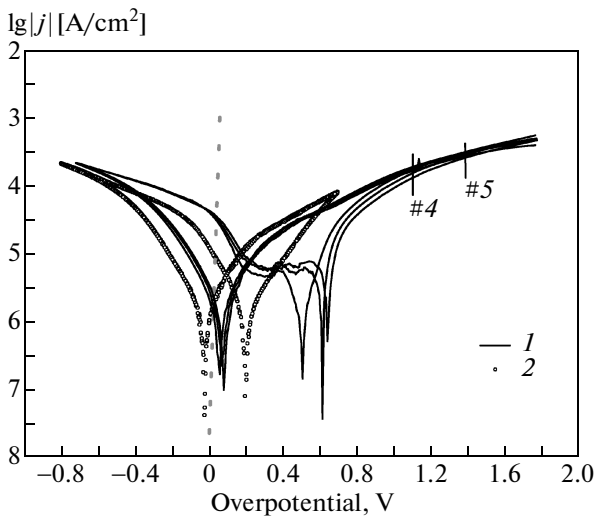


Fig. 2. Representation of the $I-U$ data from Fig. 1 in the $\log(|j|)-\eta$ coordinates (logarithm of absolute value of current vs. overvoltage on cell in the (1) of 0–2.4 V and (2) 0–1.5 V interval. The dash-dot curve corresponds to a zero-current state; markers 4 and 5 correspond to the conditions of impedance measurements in Fig. 3.

same $\log(|j|)-\eta$ coordinates by circles. A difference between the two curves is related to different intervals of the overvoltage. For the main curve 1, the interval of η [eta] is asymmetric relative to the equilibrium voltage interval of $0 < U_{\text{cell}} < 2.4$ V; that is, -0.8 V $< \eta < 1.5$ V. Curve 2 in inset (b) to Fig. 1 corresponds to a narrower but symmetric voltage interval of $0 < U_{\text{cell}} < 1.5$ V; that is, -0.7 V $< \eta < 0.7$ V. Positive η values imply an increase in the negative potential of Ge electrode and the formation (decomposition) of a hydride at the Ge–monohydrate interface. This is also manifested upon reversal of the $I-U$ curve sweep by sharp bending in the region of $U_{\text{cell}} \cong 1.4$ V on curve 1 of Fig. 1 and by a virtual equilibrium state at $\eta = 0.6 \pm 0.1$ V on curves 1 of Fig. 2. These features are rather insignificant in curve 2 of Fig. 1, for which the charge passing through the cell is smaller by one and half orders of magnitude (10 versus 0.6 mC, respectively) and, hence, the amount of hydride formed is significantly lower (these data were obtained by integrating the corresponding branches of the $I-U$ curves). According to data presented in Fig. 2, the electrochemical exchange currents at the electrode–electrolyte interfaces at 295°C can be estimated at least as 0.1 mA/cm².

The results of impedance measurements on the cell under consideration can also be explained if there is a role of hydride layer formation at the Ge–monohydrate interface as a result of a slow diffusion of hydrogen species (protons?) in the depth of the electrode. Figure 3 shows the general shape of the impedance spectrum obtained for the same cell in various states,

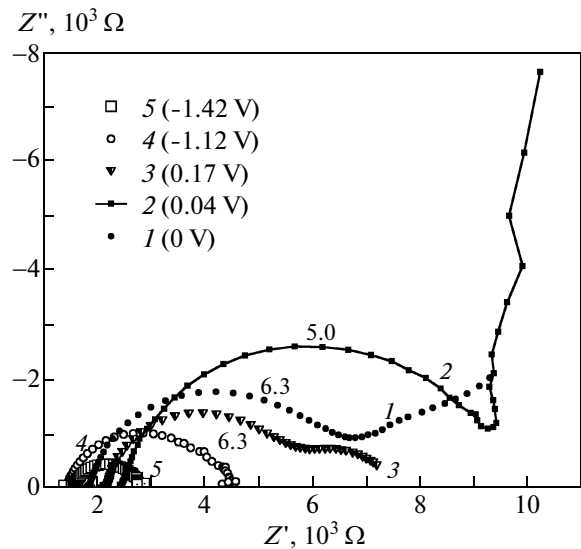


Fig. 3. Electrochemical impedance of the (+)C|KOH · xH₂O|Ge(–) type cell operating at 295°C in various regimes, measured in a frequency range of 1 mHz–2 MHz. The frequencies of Z'' maximum for curves 4 and 5 are 2.5 and 5 Hz, respectively, while those for curves 1–3 are indicated in the figure. The values of overvoltage at which the impedance was measured are listed at the corresponding curve notation.

including (i) a zero-current state ($I, \eta = 0 \pm 0.01$ V) or a close state of 0.75 V (2, $\eta = 0.04 \pm 0.005$ V), (ii) in a regime of “discharging” via external load at 0.51 V (3, $\eta = 0.17 \pm 0.02$ V), and (iii) in a regime of “charging” at 1.83 V (4, $\eta = -1.12 \pm 0.02$ V) and 2.1 V (5, $\eta = -1.42 \pm 0.02$ V). Here, the voltage on the cell is given directly (with a minus sign on Ge!) and the data in parentheses give the numbers of impedance curves in Fig. 3 and the values of overvoltage with the sign dependent on the regime. The overvoltage for curves 1–3 refers entirely to the Ge electrode, while in curves 4 and 5 only ~70% of the given overvoltage refers to the Ge electrode. Note that the employed terms correspond to the cell being treated as a rechargeable battery.

In interpretation of the electrochemical impedance spectra in Fig. 3, special attention should be devoted to curve 2 that is indicative of the presence of a capacitance in series with the electrolyte. This “capacitor” (absent in the open-circuit regime, curve 1) appears upon the application of a relatively small voltage to the cell, for which the negative potential on the Ge electrode increases in the absolute value. A high differential resistance of the cell in this regime is clearly manifested in the $I-U$ curve. This is probably related to the formation of an electric double layer involving a hydride film present at the electrode–electrolyte interface. An increase in the absolute value of the overvoltage leads to a kind of “breakdown,” after which Ge begins to operate as a metal electrode. This is also evidenced by curves 3, 4, and 5 showing a clear

tendency to vanishing of the low-frequency “tail,” as manifested by the degradation of curve 3 and spreading of the points on tails of curves 4 and 5. The later circumstance can be explained by a long duration of low-frequency impedance measurements at 0.1 Hz and below, which leads to the formation and decay of Ge hydride clusters. The correspondence of $I-U$ and impedance in Fig. 2 is indicated by the markers. Thus, the (-)Ge–potassium hydroxide monohydrate–graphite(+) heterostructure studied in this work is electrochemically active both in the thermodynamic aspect (emf \cong 0.7 V) and in the kinetic aspect (exchange currents about 0.1 mA/cm² at 295°C) (Fig. 3).

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SPELL: 1. premelting