CORROSION OF SILVER IN PERCHLORIC ACID AND THE FEASIBILITY OF USING A SILVER CHLORIDE ELECTRODE IN THE LATTER

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Silver chloride electrodes of the second kind are widely used in corrosion and electrochemical measurements as reference electrodes [1-4] (sometimes in nonaqueous media), and also as indicator electrodes in potentiometric titration and direct determination of chlorine ions in solutions [5]. In the latter case the rate of establishment of the electrode potential (which is associated with mass exchange within the porous layer) and the corrosion resistance of the electrode are important.

We have investigated electrodes made of silver foil 0.1 mm thick with a layer of porous silver on both sides, deposited by immersion in fused silver nitrate followed by heating to 500-600°C. Part of the plate (measuring 14.5 × 3 cm) was investigated as a pure silver electrode; another part (6 × 3 cm) was investigated after deposition of silver chloride – i.e., as a silver chloride electrode. The silver chloride was deposited by anodic polarization in 0.2 N hydrochloric acid with a current density of 0.3 mA/cm^2 for 4 h (current yield practically 100%). The specific mass of the coating was 1.5 mg/cm^2. The mean thickness was about 2.7 μm. The electrodes were coiled into a free spiral (to increase the surface area per unit electrolyte volume) and placed in closed glass vessels with a capacity of 18 ml (for the pure silver) or 4 ml (for the silver chloride). The electrolyte was 1 N $HClO_4$; it was prepared from double-distilled water and treble-distilled acid. To simulate the conditions of practical use of the electrodes, the solutions were not deaerated. The measurements were made at 18-20°C. The reference electrode was a hydrogen electrode in the same perchloric acid solution, which also filled the capillary (1.5-2.0 mm) electrolytic switch. The rate of transfer of metal to solution was determined without passage of an external current, potentiometrically, from the change in the potential of the test electrode (directly in the vessel) and the potential of an indicator electrode (also silver chloride) in samples of solution taken after prolonged contact with the test electrodes. In the case of the pure silver electrode, we also gravimetrically determined the mass loss of the electrode and the amount of silver in solution (the latter was found from the mass of precipitate produced by potassium chloride). The potential was measured by an ÉTs-1 high-resistance instrument taking not more than 10^{-13} A.

Table 1 shows the dynamics of the potentials of the silver and silver chloride electrodes, the concentrations of silver ions in solution, and the mean "silver solution current density" at the apparent surface.

Evidently the potential of the silver chloride indicator electrode in the solution samples taken after prolonged contact with the silver coincides, within the error of measurement, with the potential of the silver itself. This means that in the absence of an appreciable amount of chloride ions in the perchloric acid solution the silver chloride indicator electrode reacts to the changes in concentration of the silver ions like a pure silver electrode, i.e., it acts like an electrode of the first type. This conclusion is supported by the satisfactory coincidence of the data on the rate of solution of silver found by the gravimetric method (in parentheses) and by the potentiometric method. Since pure silver dissolves to an appreciable extent in the electrolyte, in the experiments with silver chloride we took measures to preserve the integrity of the silver chloride coating; for this purpose, after winding the electrode into a spiral we subjected it to additional chloriding. According to the potentiometric data, with a chlorided electrode the silver dissolved in the first 5 and next 8 days 100 times more slowly than with a pure silver one. Since the surface of the silver foil had a thin layer of porous silver, we can assume that the true rates of solution of both electrodes, converted to a smooth surface, were much lower.

Our results show that the rate of solution of pure silver is much less than the limiting ionization current of oxygen present in the solution in large excess, although its reduction at the electrode potential is quite possible. Our computations revealed that even with prolonged contact between the metal and the solution, only one

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TABLE 1

Electrode	Duration of contact with solution, h	Potential of "working" electrode, mV	Potential of indicator electrode, mV	Cl^- concentration in solution, g/liter $\cdot 10^{-3}$	Mean solution current density, A/cm^2
Silver	0	430	502–506	1,1	
	1	576	576		
	3	578	578		
	17	589	589		
	96	600	600		
	840	630	630	152	$2{,}2\cdot10^{-8}$ $(2{,}1\cdot10^{-6})$
Silver chloride	0	506	506	1,1	
	15	–	513		
	120	–	520	2,0	$2{,}0\cdot10^{-10}$
	312	533	533	3,3	$1{,}9\cdot10^{-10}$

third of the oxygen in and above the solution was expended, and if solution was limited by access of oxygen to the electrode surface, its rate would approach 1 $\mu A/cm^2$. In the case of a chloridized electrode the "preserve" oxygen exceeded the consumption several hundredfold. Evidently the rate of solution of pure silver is governed by the rate of spontaneous interaction between silver and oxygen, e.g., forming a surface oxide, and its subsequent solution in the acid, according to the overall reaction

$$2Ag+{}^1/_2O_2+2H^+=H_2O+2Ag^+$$

Since phase silver oxide dissolves in 1 N perchloric acid rapidly, we must evidently assume that chemisorbed oxygen is fairly firmly retained by the silver surface. In solutions with higher pH value, the rate of transfer of metal to solution will clearly be less than the value given above for a pure silver electrode. We must turn our attention to some properties of a silver chloride electrode in perchloric acid solutions. If the integrity of the passivating silver chloride coating is broken, the potential of the electrode slowly becomes more noble on account of solution of the exposed parts and increase in the concentration of silver ions in the adjoining volumes of solution. In this case the passivating chloridized layer can be "healed" by additional chloridizing at the above-mentioned current density in hydrochloric acid. It is interesting that immediately after this polarization the potential of even a well-washed electrode immersed in 1 N $HClO_4$ reaches 0.67 mV and decreases only gradually. Possibly the initial high value of the potential is due to a high concentration of silver ions in the surface layer as a result of chemical solution of some part of the oxidized silver with formation of $AgClO_4$ which is gradually removed to the bulk of the solution. If a "fresh" highly active chlorided electrode is kept in hydrochloric acid for 10-15 h without passing anodic current, it becomes passive relative to solution. Evidently in a hydrochloric acid solution there is a chemical reaction of the anodically formed surface oxide to form a continuous passivating film of silver chloride, which subsequently ensures normal functioning of the electrode as an indicator for the determination of chloride ions directly in the solutions. We can note that the silver chloride coating is mechanically strong: When a platinum wire electrode, the potential of which is 0.75-0.85 V in a perchloric acid solution, is in contact with silver, it acquires the potential of the latter, but when in contact with a silver chloride electrode it retains its own potential unaltered even under marked pressure. It is necessary to remove the whole of the silver chloride layer to ensure metallic contact between the silver and the platinum.

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