

Problem Concerning the Lowering of Hydrogen's Overvoltage

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STAT

OVERVOLTAGE
LOWERING THE SUPERTENSION IN HYDROGEN

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A great number of studies has been devoted to investigating possibilities of changing the discharge speed constant in hydrogen, and consequently, the possibility of changing the intensity of its ^{7/4} ~~supertension~~ ^{overvoltage} during electrolysis. Among these studies, the most interesting from the applied point of view are those dealing with the effect of the material and structure of the electrode surface on the kinetics of the electrode process. Thus, for instance, Stender and Fecharaskaya [(1)], studying the separation of hydrogen in the presence of technological current density on a series of metals and alloys, established the possibility of a sharp drop in the supertension by applying tungsten and tungsten-nickel cathodes. Positive results from the use of alloys were noted also by other authors. Kabanov and Rosentsveyg [2] discovered the relation between hydrogen supertension and the content of fixed oxygen on the surface of iron electrodes. And finally, the research on hydrogen supertension on metal electrodes with a highly developed surfaces (metalloceramics and powders) conducted by Kuzmin [3] (iron), Murtazaev [4] (cobalt) and Maytak [5] (copper), indicate great possibilities of lowering supertension by the use of highly dispersed materials as cathodes.

It seems to us that the greatest practical interest is presented by research directed toward a choice of cathode material by means of a systematic study of hydrogen supertension on dispersed electrodes obtained by different methods and from differ-

ent metals and alloys.

In our preceding works we were able to establish [6] the basic conditions for the electrolytic production of highly dispersed mono and poly-component cathode metal precipitates. The goal of this work was to establish an industrial method of obtaining metals and alloys in powder form for metalloceramics, catalysts and cementing materials in hydroelectrometallurgy.

High purity, dispersion and the high chemical activity of the products obtained gave rise to the assumption that their utilization as cathode material might lead to a sharp increase in the speed of hydrogen discharge. At the same time, the method recommended by us for the electrolytic precipitation of thin layers of dispersed metals and alloys over compact electrodes, may easily be carried out with existing devices and therefore does not entail great expense. In this connection we investigated the kinetics of the separation of hydrogen on electrolytically obtained, dispersed precipitates of Ag, Pt, Cu, Bi, Sn, Ni and Fe.

EXPERIMENTAL PART

Experimental method

The precipitates to be studied were prepared by means of electrolytic separation of the metals on a Pt-electrode. The composition of the electrolytes and the current densities are shown in Table 1. Initially, during the production of dispersed precipitates, a layer of compact metal coated the platinum electrode, then, with current densities surpassing the maximum current density of diffusion,

(D_{max}), the powder precipitated. The value of D_{max} was previously computed according to the equation corresponding to the maximum diffusion speed of the discharged ions, and was then verified experimentally. For the precipitation of bi-component dispersed systems, electrolysis was conducted with current densities higher than the value of D_{max} in order to obtain a more positive metal.

The amount of precipitated powder was the same in all instances. The duration of electrolytic precipitate coating was determined from the relation $D_t = Q \frac{Ah}{cm^2}$, which equalled 0.008-0.01.

Table 1

CONDITIONS FOR THE PRECIPITATION OF
METALS AND ELECTRICAL CAPACITY

[1] Precipitate	[2] Electrolyte Composition	[3] Current Density (in mA/cm ²)	[4] Electrical Capacity (in mF/cm ²)
Compact Cu	0.1 n. CuSO 1 n. H SO	$D_1=1.5$	35
Powder Cu	Same	$D_1=1.5; D_2=50$	1180
Compact Ag	0.005 n. NaAg(CN)	$D_1=1.5$	200
Powder Ag	Same	$D_1=1.5; D_2=50$	912
Compact Ni	0.1 n. NiSO 20 g/l (NH)SO 10 g/l NaCl	$D_1=1.5$	50
Powder Ni	Same	$D_1=1.5; D_2=50$	1025
Compact Pt	Smooth Commercial Platinum	---	---
Powder Pt	Electrolite, Platinated According to Mislovitser	(*)	1030

[1]	[2]	[3]	[4]
Compact Bi	1 n. (C H OHCH SO) Bi	D ₁ =10	92
Powder Bi	Same	D ₁ =2; D ₂ =150	910
Compact Fe	0.1 n. FeSO 20g/l (NH) SO 10 g/l NaCl	D ₁ =4	--
Powder Fe	Same	D ₁ =4; D ₂ =100	1200
Compact Sn	0.2 n. SnSO 1 n. H SO 0.3 g/l diphenylamine 0.75 g/l naphthol	D ₁ =10	35
Powder Sn	0.2 n. SnSO 1 n. H SO 1 g/l gelatin	D ₁ =10; D ₂ =100	577
Powder Fe+Ni	(0.1 n. FeSO 0.02 n. NiSO) 20 g/l(NH) SO 10g/l NaCl	D ₁ =4; D ₂ =100	1320
Powder Cu+Ag	(0.1 n. CuSO 0.02 n. Ag SO) 1 n. H SO	D ₁ =1; D ₂ =20	1250
Powder Fe+Cu	(0.1 n. FeSO 0.02 n. CuSO) 20g/l(NH) SO 10g/l NaCl	D ₁ =1.5; D ₂ =10	1100
Powder Sn+Cu	(0.2 n. SnSO 0.2CuSO) 1 n. H SO	D ₁ =1; D ₂ =50	950

(*) Current from a 4-volt Accumulator was used for five minutes

Table 2

YIELD
POTENTIALS OF HYDROGEN SEPARATION ON COMPACT AND DISPERSED METALS (*)

[1] D mA/cm ²	[2] Electrolyte in Sulphuric Acid										[3] Electrolyte 22 percent KOH			
	[A] Cu		[B] Ag		[C] Ni		[D] Pt		[E] Bi		[F] Sn		[G] Fe	
	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]	[i]	[j]	[k]	[l]	[m]	[n]
	Smooth 200 μ F	Powder 1180 μ F	Smooth 200 μ F	Powder 912 μ F	Smooth 50 μ F	Powder 1025 μ F	Smooth 1030 μ F	Powder	Smooth 92 μ F	Powder 910 μ F	Smooth 35 μ F	Powder 577 μ F	Smooth	Powder 1200 μ F
0.25	0.350	--	0.342	0.232	0.313	0.377	---	0.283	---	---	0.534	0.537	1.292	1.192
0.50	0.479	0.453	0.523	0.380	0.356	0.378	---	---	0.800	0.620	0.550	0.541	1.336	1.252
1.00	0.545	0.490	0.558	0.406	0.410	0.379	0.557	0.290	0.860	0.745	0.830	0.578	1.394	1.278
2.00	0.590	0.531	0.580	0.433	0.473	0.381	0.569	0.296	0.895	0.782	0.874	0.780	1.462	1.303
4.00	0.643	0.565	0.621	0.448	0.526	0.389	0.588	0.300	0.932	0.813	0.910	0.818	1.522	1.332
6.00	0.667	0.585	0.639	0.459	0.562	0.397	0.625	0.302	0.952	0.834	0.933	0.840	1.567	1.348
8.00	0.682	0.585	0.657	0.466	0.583	0.413	0.656	0.304	0.962	0.848	0.949	0.855	1.593	1.357
10.00	0.691	0.590	0.676	0.470	0.600	0.418	0.680	0.306	0.970	0.859	0.960	0.859	1.614	1.366

[1]	[2]														[3]	
	[A]		[B]		[C]		[D]		[E]		[F]		[G]			
	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]	[i]	[j]	[k]	[l]	[m]	[n]		
50.0	0.870	0.665	0.870	0.520	0.817	0.496	0.817	0.325	1.032	0.926	1.091	0.921	1.786	1.418		
60.0	0.860	0.662	0.889	0.532	0.847	0.504	0.834	0.328	1.040	0.934	1.126	0.930	1.801	1.428		
70.0	0.880	0.670	0.903	0.532	0.870	0.510	0.849	0.332	1.047	0.940	1.154	0.936	1.816	1.438		
80.0	0.880	0.672	0.926	0.535	0.922	0.511	0.863	0.334	1.052	0.945	1.180	0.941	1.834	1.445		
90.0	0.890	0.675	0.938	0.541	0.948	0.516	0.878	0.337	1.057	0.951	1.197	0.947	1.847	1.452		
100.0	0.900	0.679	0.950	0.544	0.974	0.522	0.892	0.340	1.060	0.960	1.220	0.950	1.863	1.458		

(*) Here and in Table 3 the values of E are given in relation to the potential of a normal calomel electrode (E=0.28) taken as zero.

[1]	[2]										[3]			
	[A]	[B]	[C]	[D]	[E]	[F]	[G]	[H]	[I]	[J]	[K]	[L]	[M]	[N]
	[a]	[b]	[c]	[d]	[e]	[f]	[g]	[h]	[i]	[j]	[k]	[l]	[m]	[n]
12.00	0.701	0.596	0.682	0.474	0.623	0.428	0.699	0.307	0.978	0.866	0.964	0.867	1.637	1.372
14.0	0.711	0.601	0.690	0.478	0.640	0.439	0.714	0.308	0.983	0.870	0.972	0.872	1.655	1.378
16.0	0.723	0.610	0.706	0.481	---	0.447	0.730	0.311	0.987	0.877	0.984	0.877	1.671	1.382
18.0	0.733	0.614	0.730	0.484	0.649	0.451	0.740	0.312	0.990	0.880	0.992	0.881	1.681	1.385
20.0	0.743	0.620	0.758	0.486	0.670	0.456	0.749	0.313	0.993	0.883	0.999	0.855	1.691	1.388
22.0	0.753	0.624	0.780	0.489	0.686	0.461	0.757	0.313	0.997	0.885	1.007	0.889	1.699	1.391
24.0	0.770	0.628	0.800	0.490	0.700	0.466	0.765	0.313	1.00	0.890	1.018	0.891	1.706	1.392
26.0	0.780	0.632	0.820	0.492	0.715	0.469	0.772	0.314	1.003	0.894	1.029	0.894	1.716	1.394
28.0	0.780	0.634	0.825	0.493	0.720	0.471	0.778	0.314	1.005	0.897	1.038	0.896	1.721	1.395
30.0	0.805	0.636	0.831	0.495	0.743	0.475	0.784	0.314	1.008	0.900	1.046	0.900	1.731	1.395
40.0	0.850	0.647	0.855	0.505	0.784	0.487	0.798	0.322	1.024	0.913	1.066	0.912	1.765	1.408

FIGURE 1

Device for the Determination of Polarization.

- (1) Hydraulic seal. (2) Cut. (3) Haber.
(4) Cathode. (5) Anodes.

The measurements were made in an electrolyzer, shown in Figure 1, made of a glass vessel containing two Pt-anodes and of an electrolytically coated Pt-cathode with $S=3 \text{ cm}^2$. The hydrogen separation potential was measured in an 1 n. solution of H_2SO_4 , or in a 22 percent solution of KOH (chemically pure). The ends of the haber came to both sides of the cathode and were pressed tightly against the metal layer. The haber, through intermediate vessels was connected with a normal calomel electrode which serve as comparison electrode.

The measurements of the potential (\bar{U}_k) were made by the direct compensation method with the help of a Raps type potentiometer built at the Stalin plant. The electrolyzer was put in a thermostat in which a constant temperature of 30 ± 0.5 degrees centigrade was maintained by an electronic relay.

Electrolytic hydrogen was piped to the electrolyzer from the bottom. In order to insure a constant hydrogen atmosphere in the instrument, the latter communicated with the outside atmosphere only by way of a hydraulic seal. The ^{overtension} supertension measurements were made during a strictly constant number of stirring rod revolutions. This was controlled by a voltmeter connected with the motor cleats.

Together with the supertension on measurements we determined the electrolytic capacity of the cathode in proportion to its actual surface. The capacity was measured upon polarization of the electrode

-- 0.6-0.8 V. The method for capacity measurement was described earlier.

DISCUSSION OF RESULTS

The research data concerning hydrogen separation potentials in 1 n. H_2SO_4 and 22 percent KOH solutions on compact metals: Pt, Bi, Ni, Ag, Sn, Cu, Fe and their dispersed precipitates, as well as on their alloys, is given in Tables 2 and 3 and in Figures 2 and 3. In all cases the values of the potentials are given in relation to the potential of a normal calomel electrode. In order to convert these figures to the hydrogen scale one must subtract 0.28 V from the Table values.

Table 3

POTENTIALS OF HYDROGEN SEPARATION ON DISPersed BI-COMPONENT
PRECIPITATES OF METALS.
ELECTROLYTE -- 1 n. H_2SO_4 AND 22PERCENT KOH. TEMPERATURE, 30°

[1]	[2]		[3]		[4]	[5]
D	Electrolyte		Electrolyte		I mA	lg I
mA/cm ²	in H_2SO_4		22 percent KOH			
	[a]	[b]	[c]	[d]		
	1250 μ F	950 μ F	1100 μ F	1320 μ F		
0.25	--	0.510	1.204	1.214	0.75	-0.125
0.50	--	0.530	1.276	1.246	1.50	+0.176
1.00	0.333	0.724	1.300	1.287	3.00	0.477
2.00	0.378	0.780	1.320	1.310	6.00	0.778
4.00	0.402	0.817	1.343	1.332	12.0	1.079

[1]	[2]		[3]		[4]	[5]
	[a]	[b]	[c]	[d]		
6.00	0.414	0.834	1.360	1.344	18.0	1.255
8.00	0.423	0.843	1.374	1.358	24.0	1.380
10.00	0.431	0.852	1.383	1.362	30.0	1.477
12.0	0.437	0.858	1.393	1.369	36.0	1.556
14.0	0.442	0.865	1.400	1.375	42.0	1.623
16.0	0.448	0.872	1.405	1.380	48.0	1.681
18.0	0.452	0.876	1.410	1.385	54.0	1.732
20.0	0.457	0.880	1.416	1.390	60.0	1.778
22.0	0.461	0.884	1.420	1.394	66.0	1.819
24.0	0.467	0.888	1.425	1.397	72.0	1.857
26.0	0.471	0.892	1.429	1.401	78.0	1.892
28.0	0.478	0.894	1.433	1.406	84.0	1.924
30.0	0.486	0.896	1.436	1.410	90.0	1.954
40.0	0.506	0.905	1.455	1.424	120.0	2.079
50.0	0.521	0.913	1.470	1.436	150.0	2.176
60.0	0.535	0.920	1.480	1.447	180.0	2.255
70.0	0.545	0.928	1.489	1.457	210.0	2.322
80.0	0.550	0.937	1.496	1.466	240.0	2.380
90.0	0.555	0.944	1.503	1.473	270.0	2.431
100.0	0.560	0.950	1.508	1.480	300.0	2.477

Examining the data in the tables we see that in all cases the hydrogen separation potential on dispersed metals and their alloys is considerably lower than on compact metals. Thus, for instance, the following values, obtained from Table 2, show that the difference between the hydrogen separation potentials on compact and dispersed silver,

when $D=100\text{mA}/\text{cm}^2$, is of 406mV, on nickel cathodes 452mV, etc..

Electrode material	Pt	Fe	Cu	Ag	Ni	Bi	Sn
$\Delta E_v = E_{\text{comp}} - E_{\text{disp}}$ when $D=100\text{mA}/\text{cm}^2$	0.552	0.405	0.221	0.406	0.452	0.100	0.270
Increase in surface $S_{\text{disp}} : S_{\text{comp}}$	--	--	35	4.5	20	10	16

Especially interesting is the fact that the drop in polarization during passage to dispersed precipitates is almost in every instance significantly bigger than would be true if only the drop in the current density were considered. In reality, let us suppose, that the relation of η to D , in accordance with the retarded discharge theory, is subject to the equation: $\eta = \alpha + 0.116 \lg D$.

Then, for the nickel cathode, for instance, the difference of H_2 super-tension on dispersed and compact electrodes must equal:

$$\eta_c - \eta_d = 0.116 \lg 20$$

while the actual difference is $\eta_c - \eta_d = 0.452\text{V}$, or approximately three times more.

FIGURE 2

H_2 Separation Potentials on Smooth and Dispersed Metals in 1 n. H_2SO_4 22 percent KOH (Fe).

- (A) D mA/cm²; Abscissa Axis -- E_p . Metals: (1) Pt_n; (2) Ni_n; (3) Ag_n; (4) Cu_n+Ag_n; (5) Cu_n; (6) Pt₂; (7) Cu₂; (8) Ag₂; (9) Ni₂; (10) Sn_n+Cu_n; (11) Sn_n; (12) Bi_n; (13) Bi₂; (14) Sn₂; (15) Fe_n; (16) Fe_n+Ni_n; (18) Fe₂.

A similar regularity is observed for Ag, Pt, Sn, and other metals. Thus a change from compact to dispersed cathodes leads to a drop in supertension not only because of an increase in the actual electrode surface, but, in a number of cases, principally because of an increase in the discharge speed constant. The latter is in good accord with the heightened chemical activity of a series of electrolytic powders in purely chemical reactions.

When a certain quantity of a more electropositive metal enters into the dispersed precipitate (bi-component system), the drop in supertension is still more significant. For instance, in changing from compact to dispersed copper, the drop of the hydrogen separation potential is:

$$E_{\text{comp. Cu}} - E_{\text{powd. Cu+Ag}} = 900 - 560 = 340 \text{ mV.}$$

The values of the potential correspond to the straight lines in the semi-logarithmic system of coordinates $E - \lg I$, and the values of the coefficient b in Tafel's formula ($\eta = a - b \lg D$) for a series of smooth metals are close to the data of Pecherskaya and Stender, giving an average of 0.10-0.12. The values of the coefficient b for smooth (compact) Ni, Fe, Cu have been found to be somewhat higher (Table 4).

See page 13 for Table 4

For the majority of dispersed metals, the value of the coefficient b is less than 0.10. This agrees well with the data of various authors who think that like retarded discharge supertension may largely be determined by other "stages" of hydrogen separation, in particular, by the retarded state of the process of recombination of the hydrogen atoms.

Table 4

VALUES OF THE COEFFICIENT b FOR THE HYDROGEN SUPERTENSION
ON DISPERSED ELECTROLYTIC PRECIPITATES

Electrode Material	Coefficient (b)	Electrode Material	Coefficient (b)
Pt	0.015	Fe+Cu	0.111
Fe	0.087	Fe+Ni	0.075
Ag	0.060	Cu+Ag	0.082
Bi	0.096	Sn+Cu	0.0945
Sn	0.091		
Cu	0.150		

The experimental material here presented shows that the employment of electrolytic coating of cathodes by dispersed metals and their alloys opens prospects for a significant drop (in certain cases up to 0.4V and more) in cathode potential in industrial processes, for example during the electrolytic production of chlorine, electrolysis of water, and others. This fact will considerably lower the consumption of electric power and, consequently, will reduce the cost of the processes.

FIGURE 3

Relation $E \sim \lg I$ for H_2 Separation. The value E_{equilib} is given for the separation of H_2 from 1 n. H_2SO_4 (0.29V in relation to a calomel electrode). B -- I (in mA); A -- E (in mV); V -- $\lg I$; G -- Equilib Metals: 1 -- Fe+Cu; 2 -- Fe; 3 -- Bi; 4 -- Bi; 5 -- Sn+Cu; 6 -- Ag; 7 -- Cu; 9 -- Ag; 10 -- Pt; 11 -- Ni.

CONCLUSIONS

(1) We studied the supertension of hydrogen in 1 n. solution of H_2SO_4 and 22 percent KOH on compact and dispersed electrolytic precipitates of Pt, Ag, Cu, Li, Sn, Ni and Fe and also on bi-component metallic systems (Cu-Ag; Sn-Cu; Fe-Ni).

(2) We showed the possibility of lowering the supertension by more than 0.4V by using certain powdery electrolytically obtained, electrodes.

(3) We established that the drop of supertension occurs not only because of the lowering of the actual current density in relation to the increase in the actual surface of the cathode, but also in great measure because of the growth in the value of the discharge speed constant of hydrogen ions.

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