USE OF CORROSION INHIBITORS IN CHEMICAL CURRENT SOURCES

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The authors discuss the theoretical principles and practical results of the use of inhibitors to increase the shelf life and service life of chemical current sources (CCS) and to improve their electrical characteristics (degree of utilization of active masses, energy efficiency, terminal voltage, etc.). They show that inhibitors must be the technical basis for realizing fundamentally new CCS with electrolytes and active masses which give high-current outputs at enhanced discharge voltages.

One of the most important shortcomings of chemical current sources (CCS) is self-discharge, largely due to corrosion processes. Corrosion reduces the service lives of CCS and impairs their electrical characteristics. Moreover, corrosion, by limiting the number of metals which can be used as anodes in CCS, is holding up progress in the development of CCS and impeding technical progress in the field. For some time, one of the solutions to this problem has been the addition of various substances, including corrosion inhibitors [1, 2], to the electrolyte and/or active masses of CCS. However, the full potential of this method has come to light only in the last two or three decades. In this article, while not claiming to make an exhaustive survey of the literature, we attempt to discuss certain aspects of the use of inhibitors in CCS, mainly in connection with the problem of effective anodes.*

1. USE OF INHIBITORS WITH THE AIM OF INCREASING THE SERVICE LIVES OF CCT AND IMPROVING THEIR ELECTRICAL CHARACTERISTICS

As a model we shall take the system

$$M|HA|MO|M \qquad (1)$$

where M is the anode material (the material of the negative electrode of the CCS), usually some electronegative metal, HA is the aqueous or nonaqueous electrolyte (a solution of an acid, salt, or base), and MO is the cathode material (the material of the positive electrode of the CCS), usually some sort of oxide. For convenience and definiteness in our discussion we shall assume that M is zinc, HA is sulfuric acid solution, and MO is lead dioxide. Then the model system can be written in the form

$$Cu|Zn|H_2SO_4,\ ZnSO_4|PbO_2|Pb|Cu. \qquad (2)$$

The behavior of this system and many of its properties can be described with the aid of the polarization diagram shown in Fig. 1. As abscissa we have plotted the potential, and as ordinate, the current density in arbitrary units, with cathodic currents (i_k) above and anodic currents (i_a) below.

In the absence of corrosion, the emf ${}_{M,MO}E_r \equiv {}_{Zn,PbO_2}E_r$ of the system is determined by the difference between the equilibrium potentials of the dioxide electrode ${}_{PbO_2}E_r$ and the zinc electrode ${}_{Zn}E_r$:

$${}_{M,MO}E_r = {}_{MO}E_r - {}_{M}E_r \equiv {}_{Zn,PbO_2}E_r = {}_{PbO_2}E_r - {}_{Zn}E_r. \qquad (3)$$

The anodic polarization curve corresponding to solution of metal,

*We shall not discuss the influence of inhibitors on the structural elements of CCS.

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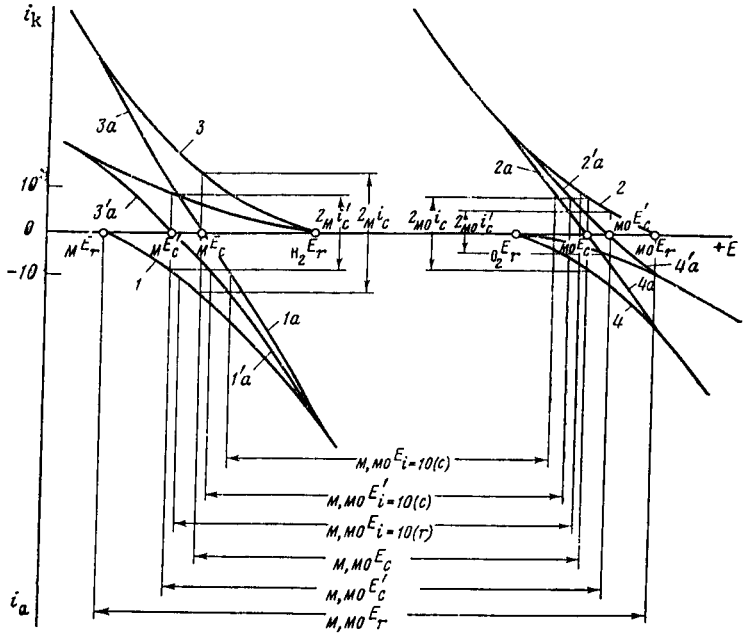

Fig. 1. Polarization diagram illustrating influence of corrosion and its inhibition on electrical characteristics of CCS of the type M/HA/MO/M and its durability. For interpretation of curves and notation, see Appendix.

$$Zn=Zn^{2+}+2e^-, \tag{4}$$

coincides with curve 1 in Fig. 1, and the cathodic curve, corresponding to reduction of lead dioxide,

$$PbO_2+2e^-+2H^++H_2SO_4=PbSO_4+2H_2O\,, \tag{5}$$

coincides with curve 2. During discharge of the cell by some current i = 10 (in arbitrary units),* the working voltage of the system will correspond to the quantity $_{M,MO}E_{i=10}$ (see Fig. 1), which is less than the emf of the system $_{M,MO}E_r$; the masses of the two electrodes are expended in conformity with reactions (4) and (5), and all the electrons pass through the external circuit of system (2) from the left-hand electrode to the right-hand one, i.e., they all take part in the generation of current. When not in operation, e.g., during storage, the active mass should not be expended and there should be no energy loss. Then the degree of utilization of the active mass should be unity, and the storage life can be as long as you like. However, in real conditions at each of the electrodes there are not only the principal current-forming reactions but also conjugated reactions: at the negative electrode, reactions of reduction (curve 3), and at the positive electrode, of oxidation (curve 4), e.g.,

$$2H^++2e^-=H_2; \tag{6}$$

$$H_2O=\tfrac{1}{2}O_2+2H^++2e^-. \tag{7}$$

As a result, not all the electrons liberated at the anode by reaction (4) go into the external circuit; some of them combine with electron acceptors at the electrode itself, e.g., with hydrogen ions by reaction (6). In other words, a certain proportion of the zinc is not dissolved by reaction (4) but by the reaction

$$Zn+2H^+=Zn^{2+}+H_2, \tag{8}$$

i.e., unproductively, without liberating electrons or supplying current to the external circuit. Reaction (8) naturally continues even when no current is being taken from the system, i.e., in the inoperative state, e.g., during shelf storage. Combination of electrons by reaction (6) leads to a shift in the potential of the metallic electrode toward the positive to the corrosion potential $_M E_c$. In the absence of an external current, i.e., at

*In constructing Fig. 1, we have assumed that the geometrical surface areas of the cathode and anode are the same and are equal to unity, i.e., I = i (the current is equal to the current density). This assumption is not critical, and can be abondoned, though the construction and arguments would then become somewhat more complicated.

the corrosion potential, the rates of solution of zinc and of evolution of hydrogen (in current units) are both equal to the corrosion current of the metal (see Fig. 1):

$$({}_{M}i_{a}={}_{H_2}i_{k}={}_{M}i_{c})_{E={}_{M}E_{c}}. \tag{9}$$

In this case the corrosion current ${}_{M}i_{c}$ also characterizes the rate of self-discharge of the negative electrode of the CCS. Similarly, as a result of the self discharge of the positive electrode, its potential changes in comparison with its reverse value, and ${}_{MO}E_{c}$ will be more negative than ${}_{MO}E_{r}$. Owing to self discharge, the voltage of the cell at i = 0,

$${}_{M,\,MO}E_{c}<{}_{MO}E_{c}-{}_{M}E_{c}\,, \tag{10}$$

will be less than its emf in the absence of corrosion (see Fig. 1):

$${}_{M,\,MO}E_{c}<{}_{M,\,MO}E_{r}.$$

In exactly the same way, the working voltage of the cell will be reduced when some current is being taken (e.g., if i = 10):

$${}_{M,\,MO}E_{c(i=10)}<{}_{M,\,MO}E_{r(i=10)}. \tag{10a}$$

Since during the shelf life of the cell its electrodes corrode at a rate of ${}_{M}i_{c}$ for the anode and ${}_{MO}i_{c}$ for the cathode, there is a continual loss of capacity, and this is one of the causes of self discharge of the source. The capacities of both the electrodes will be completely lost after times τ_k and τ_a, given by the equations

$$\tau_{k}=\frac{Q_{k}}{{}_{MO}i_{c}}; \tag{11}$$

$$\tau_{a}=\frac{Q_{a}}{{}_{M}i_{c}}, \tag{12}$$

where Q_k and Q_a are the capacities of the active masses of the cathode and anode in ampere-hours.* Corrosion reduces the degree of utilization of the active masses, and decreases the proportion of the current given out by them to the external circuit, i.e., the useful proportion of the current ξ. Thus for the negative electrode (anode) at some potential E the useful proportion of current is given by

$$\xi=\left(\frac{{}_{M}i_{a}-{}_{H_2}i_{k}}{{}_{M}i_{a}}\right)_{E}=1-\left(\frac{{}_{H_2}i_{k}}{{}_{M}i_{a}}\right)_{E}. \tag{13}$$

When $E = {}_{H_2}E_r$, from Fig. 1 it follows that $i_k = \vec{i}_{H_2} - \overleftarrow{i}_{H_2} = 0$ and $\xi = 1$, i.e., the whole of the current goes into the external circuit. When $E = {}_{M}E_c$, ${}_{H_2}i_k = {}_{M}i_a$ then $\xi = 0$, i.e., the whole of the current is expended in the corrosion process. If the electrode potential lies between ${}_{M}E_c$ and ${}_{H_2}E_r$, $0 < \xi < 1$, and the less the retardation of the hydrogen evolution process, the less is ξ.

Thus corrosion of the electrodes reduces the emf and the effective voltage of the CCS, shortens its shelf and service lives, and reduces the degree of utilization of the active masses, and thus decreases the useful proportion of current. All these harmful consequences of corrosion can be avoided or reduced by means of the appropriate corrosion inhibitors. In current sources, together with the general requirements for all inhibitors [3, 5], corrosion inhibitors must also meet special requirements specific to the protected system in question [2, 5]. One of the principal conditions which must be satisfied by inhibitors for CCS is selective action on the particular reactions on which the corrosion process is based. The inhibitor must primarily (in the limit, exclusively) suppress the conjugate reaction, in our case the evolution of hydrogen at the negative electrode and oxygen at the positive, without affecting the main reaction of ionization of metal or reduction of oxide.†

When such inhibitors are added, there is an increase in the overvoltages of both hydrogen and oxygen, so that the stationary potentials shift toward the negative for the anode and toward the positive for the cathode

*The useful life of the cell is less than the time for complete loss of its capacity or of the capacity of at least one of the electrodes, because it does not relate to complete loss of capacity but only to its reduction to a level at which the cell can no longer be used. Moreover, self-discharge of the cell can be caused by other factors.

†Among other requirements imposed on inhibitors for CCS we must include stability at any values of the effective electrode potentials. Moreover, while improving the action of one electrode, the inhibitor must not harm that of the other.

($_{M}E'_{c}$ and $_{MO}E'_{c}$ in Fig. 1) in comparison with a source with no inhibitor. As a result of this change in the stationary potentials, there is an increase in the potential developed by the cell when the external circuit is open; i.e., at i = 0 it is now

$$_{M,\,MO}E_c' = {}_{MO}E_c' - {}_{M}E_c' \tag{14}$$

and is greater than the corresponding quantity in the absence of inhibitor (see Fig. 1). Similarly, the effective voltage when current is being taken (e.g., i = 10),

$$_{M,\,MO}E_c'{}_{(i=10)} = {}_{MO}E_c'{}_{(i=10)} - {}_{M}E_c'{}_{(i=10)}, \tag{14a}$$

will be greater after addition of the inhibitor, i.e., $_{M,MO}E'_{c}(i=10) > {}_{M,MO}E_{c}(i=10)$.

Moreover, since the corrosion rate of each electrode ($_{M}i'_{c}$, $_{MO}i'_{c}$) decreases on addition of inhibitor in comparison with the original values ($_{M}i_{c}$, $_{MO}i_{c}$, see Fig. 1), the rate of self discharge decreases, and the service life increases in proportion to the increase in the time of self discharge:

$$\tau_k' = \frac{Q_k}{{}_{MO}i_c'}; \tag{11a}$$

$$\tau_a' = \frac{Q_a}{{}_{M}i'_c}. \tag{12a}$$

The coefficients of utilization of the active masses in the presence of inhibitor will be greater than in its absence (naturally, in the electrode potential ranges in which the corrosion effect appears and in which the inhibitor preserves its action – see Fig. 1).

Thus the use of inhibitors enables us to increase the service life of a CCS and to improve all its electrical characteristics.

This conclusion is supported by the experimental data so far obtained. It has been found that in the presence of tetrabutylammonium sulfate the self discharge of a zinc electrode in a lead–zinc sulfuric-acid cell is reduced and the shelf lives of these cells in the filled state are increased severalfold [1, 6]. A beneficial effect is also obtained by adding ascorbic acid [7] and certain monocarboxylic acids containing at least two ethanolamide radicals [8]. In the electrolyte of the same cell, a combined additive (an organic substance and a heavy-metal salt) increases the discharge time by a factor of three [9].

Certain inhibitors (e.g., hydroxynaphthoic acids, N-phenylanthranilic acid, lignin, etc.), sometimes in combination with extenders, prevent oxidation of spongy lead during air-drying [10-16] and can increase the capacities of negative plates of lead storage cells by 20-50% in comparison with uninhibited cells [17].

The action of inhibitors cannot be attributed merely to a reduction in the corrosion rate on account of suppression of reactions which cause corrosion of the electrodes. It also involves positive influence on the morphology of the electrodes, not expressible on the polarization diagram. This manifestation of inhibitory action is particularly important for reusable current sources such as accumulators. In such sources the electrodes are spongy, with large specific surface area. During successive processes of charging and discharging of the electrodes (e.g., spongy zinc electrodes) there is compaction and some change of shape, reducing the number of possible working cycles and reducing the capacity of the source. The use of inhibitors, in particular polyethoxylated aliphatic and phenolic hydroxyl compounds [18-20], which are adsorbed in the same range of potentials in which a zinc electrode charges [21], preserves the desired structure and avoids loss of capacity [18-22]. Additives have been suggested which have a beneficial influence on the morphology of the positive electrodes of lead accumulators [23, 24] and increase the capacity at low temperature without reducing the service life (see, e.g., [1]).

During charging of accumulators, metallic dendrites not infrequently form, causing short circuits and damage to the cell. Dendrite formation and growth can be stopped if to the electrolyte we add certain inhibitors in concentrations depending on their nature and on the deviation of the electrode potential from the equilibrium value [25]. Thus when η_{Zn} = 100 mV, addition of a lead salt is effective at concentrations $c \geq 10^{-4}$ M; at lower concentrations the inhibitor does not affect dendrite formation or growth. Tetrasubstituted-ammonium bromides and iodides also suppress dendrite formation in concentrations of order 10^{-3} M. The commercial inhibitors "Emulphogen," "Triton," and "Igepol" are somewhat less effective in this respect.

The action of all inhibitors involves adsorption on the metal, leading to blocking of the surface and to changes in the reaction kinetics (changes in the double layer structure, the diffusion potential, and the distance between the discharge plane and the boundary [26], and also in the activity coefficient of the transitional

complex [27]). One or other effect will predominate according to the nature of the inhibitor.

2. USE OF METAL CORROSION INHIBITORS AS A BASIS FOR TECHNICAL REALIZATION OF NEW CURRENT SOURCES

The use of zinc anodes in chemical current sources, e.g., in manganese–zinc cells (MZC), has become technically possible only owing to amalgamation, i.e., to the use of mercury as a corrosion inhibitor (mercury compounds such as mercuric chloride can undergo contact reduction in MZC on the electrode surface, forming metallic mercury, and can thus act as proinhibitors [31]). Owing to the toxicity of mercury and its compounds, this type of protection is not a terribly good idea. The use of mercury as an inhibitor in attempts to replace zinc by a more electronegative metal such as aluminum did not give the desired effect. It was found that, although the hydrogen overvoltage increases and the potential of the aluminum shifts toward the negative, its corrosion rate not only fails to decrease, but on the contrary increases [29].* Other inhibitors have been suggested, but have proved ineffective [30, 31]. Subsequently much work was done, mainly by Indian scientists, to find the most suitable corrosion inhibitors for aluminum used as an anode in CCS with neutral (salt), acid, or alkaline electrolytes [32–35]. It cannot be said that they were very successful in solving the problem of replacing zinc by aluminum and of creating better CCS, but their results were very encouraging. It turned out that very many organic substances with various chemical compositions and molecular structures (amino acids [35, 37], ketones, esters [36], etc.) reduce the corrosion rate of aluminum in solutions of acids (1 M HCl). However, in these media aluminum cannot be used as an effective CCS anode, owing to its insufficiently negative potential and easy passivability. The creation of new, better current sources will no doubt involve a change not only to different materials for the anode and cathode but also to different electrolytes. Solution of the problem of obtaining high currents from sources often involves correct choice of electrolyte, and these are usually more aggressive in corrosion than those in present use. For example, in anodic solution of zinc in acids and alkalies, greater currents can be obtained at the same potentials than in salt media. It is therefore expedient and necessary to add inhibitors to the CCS, not only to use new active masses, but also in connection with the use of new electrolytes with greater corrosion activity.

In alkaline media (1 M KOH, 1 M NaOH), which are the best to use in conjunction with aluminum in current sources, all the above additives either scarcely slow up corrosion, or even slightly accelerate it [35, 36, 38]. But if to the alkali we add not only the organic substance but also a calcium salt (10^{-4} M), the position is completely altered [28–36, 38]. The inhibiting capability of the organic substances is then increased tenfold. The calcium ions themselves also possess some inhibiting action [33, 35, 39], but this is markedly increased in the presence of organic substances, i.e., we are dealing with a case of synergism. For example, in a 1 M solution of NaOH, addition of 10^{-4} M dibenzylsulfoxide gives a negative degree of protection of 1%, i.e., it slightly accelerates the corrosion; addition of a calcium salt in a concentration of $7.8 \cdot 10^{-3}$ g/liter of Ca^{2+} gives 63% protection of aluminum; but the simultaneous presence of both substances gives 82% protection [38]. The absence of any appreciable influence of organic substances on the corrosion of aluminum in alkali and the attainment of a high degree of protection when they are added together with calcium ions is explained by Remakrishnaiah and Subramanyan [38] in the spirit of the theory of Antropov [40] which is based on the concept of a corrected scale of potentials.

On the other hand, in acid media calcium ions are totally ineffective. The degree of protection (maximum 82%) attained in alkali solutions with added organic substances and calcium ions is insufficient for the operation of dry cells, but apparently satisfies the requirements for the anodes of standby (fillable) cells, especially with intensive discharge with current densities of over 0.01 A/cm^2 [31].

CONCLUSIONS

1. The use of rationally selected corrosion inhibitors can improve the main operational characteristics of chemical current sources and prolong their service lives.

2. The use of effective corrosion inhibitors is one of the principal prerequisites for the creation of new, better chemical current sources.

*However, there is one report [28] that cells with an anode of commercial aluminum (Indian mark 2S) in 15% $MnCl_2$ in combination with a cathode of manganese dioxide have better characteristics than ordinary Leclanché cells.

APPENDIX

1) Idealized polarization curve of anodic reaction, e.g., reaction of solution of zinc,

$$Zn=Zn^{2+}+2e^-, \quad (1)$$

not complicated by process of corrosion of metal.

2) Idealized polarization curve of cathodic reaction, e.g., reaction of reduction of lead dioxide,

$$PbO_2+2e^-+2H^++H_2SO_4=PbSO_4+2H_2O, \quad (2)$$

not complicated by corrosion (self-discharge) process.

3) Idealized polarization curve of evolution of hydrogen:

$$2H^++2e^-=H_2 \quad (3)$$

4) Idealized polarization curve of evolution of oxygen:

$$H_2O=2H^++{}^1/_2O_2+2e^- \quad (4)$$

1*a*, 1'*a*) Real (resultant) polarization curves of anodic solution of metal, e.g., zinc, reflecting effect of corrosion, i.e., superimposition of reaction (3) on reaction (1); here and below a prime (') will refer to solution with inhibitor.

2*a*, 2'*a*) Real (resultant) polarization curves of cathodic reduction of oxide, e.g., lead dioxide, reflecting effect of self-solution (corrosion), i.e., superimposition of reaction (4) on reaction (2).

3*a*, 3'*a*) Real (resultant) polarization curves of cathodic evolution of hydrogen, reflecting superimposition of reaction (1) on reaction (2).

4*a*, 4'*a*) Real (resultant) polarization curves of evolution of oxygen, reflecting superimposition of reaction (2) on reaction (4).

$_M E_r$: Equilibrium potential of metal (zinc).

$_{MO}E_r$: Equilibrium potential of oxide (lead dioxide).

$_M E_c$ and $_M E'_c$: Stationary potentials of metal (zinc).

$_{MO}E_c$ and $_{MO}E'_c$: Stationary potentials of oxide (lead dioxide).

M^{ic} and $M^{ic'}$: Rates of corrosion of metal (zinc) at $_M E_c$ and $_M E'_c$ respectively.

MO^{ic} and $MO^{ic'}$; Rates of self-discharge (corrosion) of oxide (lead dioxide) at $_{MO}E_c$ and $_{MO}E_c'$ respectively.

$M,_{MO}E_r$: Electromotive force of system M/HA/MO/M in absence of corrosion.

$M,_{MO}E_c$ and $M,_{MO}E'_c$: Voltage of M/HA/MO/M system on open circuit (i = 0) during corrosion process.

$M,_{MO}E_{i=10(r)}$, $M,_{MO}E_{i=10(c)}$, and $M,_{MO}E'_{i=10(c)}$: Voltages of system when current of 10 arbitrary units is taken off in the absence of corrosion, in the presence of corrosion, and with inhibition, respectively.

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