



# Passivation of zinc in alkaline solution effected by chromates and $\text{CrO}_3$ –graphite system

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## Abstract

Electrochemical properties of porous zinc electrode in alkaline solution have been modified by the additive of chromium compounds such as chromates and  $\text{CrO}_3$ –graphite system. Insertion of chromates inside the zinc electrode caused the limited solubility of the anodic dissolution products and their retention in the electrode interior. Different behaviour of the passivated zinc electrode was observed depending on cation of the used chromate. The improvement of cyclic performance of zinc has also been noted after the electrode is admixed with  $\text{CrO}_3$ –graphite system containing intercalated/incorporated oxide. Electrochemical properties of zinc electrode strongly depend on the way of chromium insertion to active material of anode. Anodic and cathodic charges have been measured during potentiodynamic cycles for the observation of passivating effect. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The redistribution of zinc material, i.e., shape change of electrode, as well as growth of zinc dendrites, irreversible passivation and electrode densification are important factors limiting the cycle life and performance of accumulators with zinc anode in alkaline solution. These problems can be partly overcome by improvement in separation and by special additives to the zinc electrode. Enhancement of the zinc electrode cycleability depends mainly on the limitation of solubility for zincate products formed during the anodic dissolution. Different methods have been applied to limit a zincate solubility and to protect their diffusion to the bulk solution. Some of these methods are as follows: (A) Application of the electrolyte with a lower alkaline concentration (2–4 M KOH) and of mixed composition, e.g., KOH, KF,  $\text{H}_3\text{BO}_3$ ,  $\text{K}_2\text{CO}_3$ , LiOH [1–4]; (B) usage of carbon additives to electrode, e.g., fine colloidal graphite [5], acetylene black [6], that accelerate the precipitation of reaction products and their retention in the interior of porous electrode as well as improve the electrical conductivity of electrode material; (C) addition of calcium oxide [7] or calcium hydroxide [8] to the zinc

electrode that form an insoluble Ca–zincate complex during the cell performance.

The solubility of zinc species in moderately alkaline electrolytes is a few times lower than in concentrated alkaline solutions. Especially, the ternary KOH–KF– $\text{K}_2\text{CO}_3$  electrolyte decreases the rate of zinc electrode shape change with only very limited capacity loss. The cycle-life performance of cells with such a mixed electrolyte was significantly improved. Limitation of zinc solubility is realized by formation zincate species or zinc-anion reaction products. Such additives as calcium hydroxide are more effective if they are incorporated into the electrode material than only added to the electrolyte. All these methods change to some extent the mechanism of zinc dissolution from the heterogeneous into solid state type. For this reason the limitation of zinc solubility and controlled passivation are the promising way for improvement of zinc electrode performance during cycling.

Passive films formed on the zinc electrode can have an active character, i.e., they undergo the further dissolution, especially if they consist of the semiconducting films of ZnO type  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  with the porous structure. However, the passivation can proceed irreversibly if inactive ZnO of compact structure and high electric resistivity is formed. Such a dense film completely blocks the anodic dissolution of zinc. Because only the passive films susceptible to

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reactivation during the reduction process fulfil the demands for cyclic performance, the choice of a suitable additive with a proper passivation effect has a great significance. Investigations of zinc passivation reported by Bass et al. [9] were devoted to additives such as borates and chromates into alkaline solution. However, their experiments were performed on the polycrystalline zinc, i.e., in conditions differing significantly from our measurements carried out using the powder-type electrodes. Some studies on the corrosion of zinc in alkaline solution after passivation in a chromic phosphate solution [10] and the influence of sulphur containing anions on the anodic behaviour of zinc [11] can be helpful for elucidation the phenomenon occurred in the secondary zinc anode treated by different additives.

In the present work, passivation of porous Zn electrode was controlled by different chromium compounds, i.e., chromates and CrO<sub>3</sub>–graphite system, as additives to electrode. Chromates of different solubility were taken into examination to influence the passivating properties of the system. Sodium and potassium chromates are known as anodic inhibitors of corrosion, i.e., substances which cause the decrease of corrosion rate. Anodic inhibitor increases the overvoltage of anodic polarization and the corrosion potential is shifted towards more positive values. Chromate anions can partially oxidize the corrosion products changing them into compounds of smaller solubility. Inhibitor based on chromates can be incorporated into the passive film, which contains chromate as well as chromium oxide, Cr<sub>2</sub>O<sub>3</sub>. Electrochemical properties of porous Zn electrode were investigated in the presence of different chromates such as BaCrO<sub>4</sub>, SrCrO<sub>4</sub>, K<sub>2</sub>CrO<sub>4</sub>. Passivation phenomenon, reactivation and ability for reduction and oxidation were especially considered.

The results of studies on chemical and electrochemical properties of graphite intercalation compounds intercalated with chromium trioxide (CrO<sub>3</sub>–GICs) [12–16] encouraged us to use this system as additive to the zinc electrode. It has been expected that CrO<sub>3</sub>–GIC, containing chromium oxides both intercalated between the graphene layers and encapsulated within the defects of unreacted graphite, can simultaneously play the role of an passivating agent and electrical collector.

Controlled passivation effect favouring the topochemical process of anodic zinc dissolution can limit both the change of electrode shape and the tendency to dendrite formation during cycling. Finally, such a modification resulting in the improvement of durability of the zinc electrode could be beneficial for practical application in accumulators.

## 2. Experimental

For the investigation of electrode–electrolyte interface, three electrode system with a Luggin capillary and a

Table 1

The effect of additives on the rest potential,  $E_r$ , of Zn–ZnO electrodes

Composition of electrode	$E_r$ vs. Zn(Hg)
Zn + ZnO	0.062 V
Zn + ZnO + 5% K <sub>2</sub> CrO <sub>4</sub>	0.075 V
Zn + ZnO + 10% K <sub>2</sub> CrO <sub>4</sub>	0.085 V
Zn + ZnO + 30% K <sub>2</sub> CrO <sub>4</sub>	0.090 V
Zn + ZnO + 1% SrCrO <sub>4</sub>	0.075 V
Zn + ZnO + 5% SrCrO <sub>4</sub>	0.156 V
Zn + ZnO + 10% SrCrO <sub>4</sub>	0.173 V
Zn + ZnO + 20% SrCrO <sub>4</sub>	0.540 V
Zn + ZnO + 30% SrCrO <sub>4</sub>	0.655 V
Zn + ZnO + 5% BaCrO <sub>4</sub>	0.090 V
Zn + ZnO + 10% BaCrO <sub>4</sub>	0.095 V
Zn + ZnO + 30% BaCrO <sub>4</sub>	0.075 V
Zn + ZnO + 5% A2–W2	0.064 V
Zn + ZnO + 10% A2–W2	0.048 V
Zn + ZnO + 30% A2–W2	0.034 V

parallel set of electrodes was applied. The pressed pellet containing 50 mg of Zn and 50 mg of ZnO with chromate or CrO<sub>3</sub>–graphite additives was a working electrode (Tables 1 and 2). Zinc powder takes the shape of spheroidal grains of 40 μm diameter whereas the diameter range of ZnO particles is from 0.2 to 0.5 μm [6]. Theoretical capacity of a fresh prepared electrode (free of additives and without additional charging) is 147.5 mA h. Electrochemical system Ag–Ag<sub>2</sub>O was used as a counter electrode and an amalgamated zinc sheet (–1.23 V vs. SHE) as a reference. Potentials throughout the paper are quoted against this electrode. The experiments were performed in the electrolyte solution 7 M KOH + 0.6 M ZnO. All the reagents were analytical grade of purity.

The potentiodynamic measurements of all the electrodes were performed with a scan rate 1 mV s<sup>–1</sup>. Starting at the rest potential of the electrode, this parameter was changed in the negative direction until a potential of –200 mV, close to the hydrogen evolution, was reached. Then the

Table 2

Anodic charges measured for Zn–ZnO electrodes during four potentiodynamic cycles

Content of electrode	Charge
Zn + ZnO	135.5 C
Zn + ZnO + 5% K <sub>2</sub> CrO <sub>4</sub>	112.6 C
Zn + ZnO + 10% K <sub>2</sub> CrO <sub>4</sub>	106.8 C
Zn + ZnO + 30% K <sub>2</sub> CrO <sub>4</sub>	51.5 C
Zn + ZnO + 1% SrCrO <sub>4</sub>	104.6 C
Zn + ZnO + 5% SrCrO <sub>4</sub>	53.5 C
Zn + ZnO + 10% SrCrO <sub>4</sub>	75.8 C
Zn + ZnO + 20% SrCrO <sub>4</sub>	33.5 C
Zn + ZnO + 30% SrCrO <sub>4</sub>	42.5 C
Zn + ZnO + 5% BaCrO <sub>4</sub>	90.8 C
Zn + ZnO + 10% BaCrO <sub>4</sub>	87.0 C
Zn + ZnO + 30% BaCrO <sub>4</sub>	89.6 C
Zn + ZnO + 5% A2–W2	120.8 C
Zn + ZnO + 10% A2–W2	128.5 C
Zn + ZnO + 30% A2–W2	107.4 C

direction of polarization was reversed and the potential was increased in the positive direction up to 2000 mV (the oxygen evolution). Potentiostat EP 20A and voltage generator EG 20 (Elpan) were applied for the potentiodynamic measurements. Anodic and cathodic charges during the electrochemical processes were measured by integrator Wenking EVI 80 (Bank Elektronik).

Barium and strontium chromates were prepared in our laboratory by the precipitation method from their salts at the strictly controlled reaction environment and solution temperature [17]. Precipitates were carefully washed with water to remove chlorides and then dried at 130°C. Morphology of chromates was studied using a JSM 35 JEOL scanning electron microscope.

CrO<sub>3</sub>-GIC designated A2-W2 throughout the paper was prepared by the impregnation-dry method described in detail previously [12,15]. Flaky graphite (99.7 wt.% C, designated A2) from Graphitwerke Kropfmühl, composed of flakes ranging in diameter from 170 to 283 μm was used as host material. Chemical formula estimated for sample A2-W2 was C<sub>59</sub>CrO<sub>3</sub> [15]. The compound examined in the present work belongs to GICs of the ash-tray structure which means that the graphite flakes are intercalated only at their peripheries (the depth of intercalation is about 20–30 μm) whereas more inner regions of flakes are free of intercalate [12].

### 3. Results and discussion

Passivation phenomenon of zinc electrode was investigated in the presence of three Cr compounds: barium, strontium and potassium chromates. Taking into account that the passivation effect is strongly depended on the concentration of passivating agent, i.e., CrO<sub>4</sub><sup>2-</sup>, the solubility product *L* and solubility in water for all the used chromates was considered [18]. The *L* value for potassium chromate was estimated from the solubility data. The *L* values differ significantly depending on the cation of chromate and are as follows: K<sub>2</sub>CrO<sub>4</sub> = 10.5; SrCrO<sub>4</sub> = 3.6 × 10<sup>-5</sup>; BaCrO<sub>4</sub> = 1.2 × 10<sup>-10</sup>. Consequently, the solubility of these compounds in water is extremely different and the highest value is for K<sub>2</sub>CrO<sub>4</sub>. K<sub>2</sub>CrO<sub>4</sub> = 62.9

g/100 g; SrCrO<sub>4</sub> = 1.2 × 10<sup>-1</sup> g/100 g; BaCrO<sub>4</sub> = 4.4 × 10<sup>-4</sup> g/100 g.

Before the potentiodynamic experiments, the rest potentials, *E<sub>r</sub>*, of the zinc electrode with different content of additives were determined. The *E<sub>r</sub>* values start to become stable about a few minutes after pouring the cell with the electrolyte (Table 1).

Due to the porous construction of electrode and possible inhomogeneity of all the components one can expect some scatter of rest potentials of electrodes, even for the same composition. In addition, amalgamated zinc sheet used as a reference representing an electrode with limited reversibility can contribute to small deviation in the rest potentials. However, the difference between the rest potentials of a blank Zn-ZnO electrode and of the electrodes containing chromate appeared too large to be accounted for by the mentioned reasons. In such a case the changes in the rest potential can be attributed to the influence of additives. From comparison of *E<sub>r</sub>* (Table 1), a great shift of the rest potentials towards more positive values is observed for the electrodes with the SrCrO<sub>4</sub> additives. For example, *E<sub>r</sub>* = 0.075 V for zinc electrode with 1% SrCrO<sub>4</sub> whereas with 5% of SrCrO<sub>4</sub>, *E<sub>r</sub>* = 0.156 V. A very great shift of the potential to the value of 0.655 V is effected by 30% of SrCrO<sub>4</sub> additive. Such a shift of *E<sub>r</sub>* cannot be exclusively elucidated by the formation of different types of zinc oxide. The mixed potential of the Zn-ZnO-Zn(OH)<sub>2</sub>, Zn-Cr<sub>2</sub>O<sub>3</sub>-CrO<sub>4</sub><sup>2-</sup> and CrO<sub>2</sub><sup>-</sup>-CrO<sub>4</sub><sup>2-</sup> system is likely responsible for these changes. No less important seem to be the size and morphology of chromate particles. The size of smooth K<sub>2</sub>CrO<sub>4</sub> polycrystals (30–150 μ) (Fig. 1a) is about two orders of magnitude larger than that of the ZnO particles. In such a case chromate grains in the mixture electrode are surrounded by ZnO particles. Due to the reaction involving ZnO and K<sub>2</sub>CrO<sub>4</sub> the barrier of base chromates type K<sub>2</sub>CrO<sub>4</sub> · ZnCrO<sub>4</sub> · Zn(OH)<sub>2</sub>, with solubility lower than that of the original K<sub>2</sub>CrO<sub>4</sub>, formed near the chromate grain surface, makes dissolution of chromate difficult. As a consequence, a relatively slow formation of passive layer onto the zinc particles occurs. This mechanism can govern not only the *E<sub>r</sub>* value but also the cyclic behaviour of the electrode. According to this interpretation, one can presume a considerable passivation effect

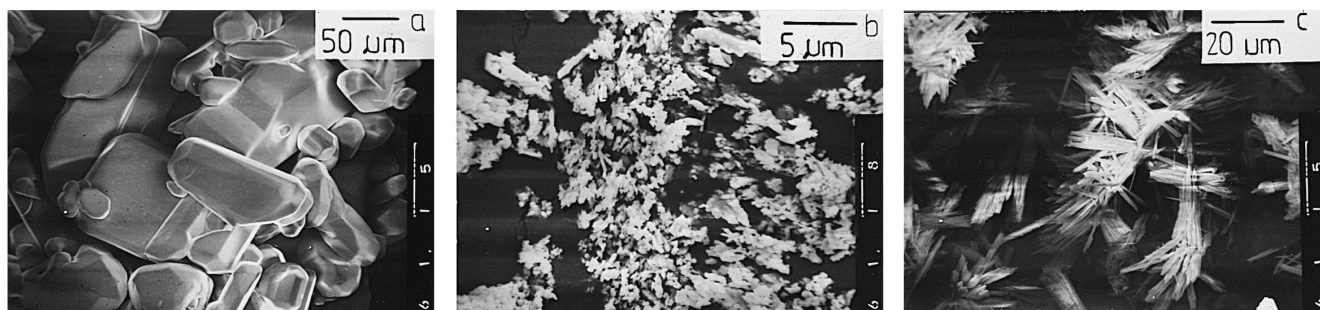


Fig. 1. Scanning electron micrographs of (a) K<sub>2</sub>CrO<sub>4</sub>, (b) BaCrO<sub>4</sub>, (c) SrCrO<sub>4</sub>.

after the content of  $K_2CrO_4$  in the electrode mixture attains suitably high level. Experimental data listed in Table 2 agree with such an expectation. A sharp decrease in charge of electrode is not observed before a large amount of 30%  $K_2CrO_4$  is added to the electrode mixture. The mechanism of passivation is quite different for  $BaCrO_4$  of an extremely low solubility. In the case of electrode with this chromate the concentration of  $CrO_4^{2-}$  is not sufficient to change the potential of Zn–ZnO electrode (Table 1). Although  $BaCrO_4$  composed of very fine and porous particles was used (Fig. 1b) the charge of electrode remains roughly constant for the whole range of the additive content (Table 2). Barium hydroxide of a low solubility, co-produced in the passivation reaction, can to some extent hinder the formation of passive film on the zinc particles. Intermediate solubility of strontium chromate and strontium hydroxide creates in zinc electrode the suitable conditions for the formation of passive film. In this case, the bigger amount of chromate, the greater shift of the rest potential. Very thin needle-shaped particles of  $SrCrO_4$  (Fig. 1c) make dissolution easier and allow an uniform concentration of chromate ions at the Zn–electrolyte interface ( $SrCrO_4$  needles are comparable in diameter with the ZnO particles whereas their length is smaller than the diameter of zinc spherules).

The potentiodynamic measurements pointed out a various influence of chromate additives on the anodic dissolution of zinc. During subsequent four potentiodynamic cycles anodic and cathodic charges of electrodes were measured. The values of charge for all the mixture electrodes are presented in Table 2. The charge measured for pellet zinc electrode was equal to 147.5 C. Because this number is in good agreement with that calculated for anodic dissolution of 50 mg of pure Zn powder, cathodic reduction of zinc oxide in our potentiodynamic experiments can be excluded. The results of performed experiments pointed

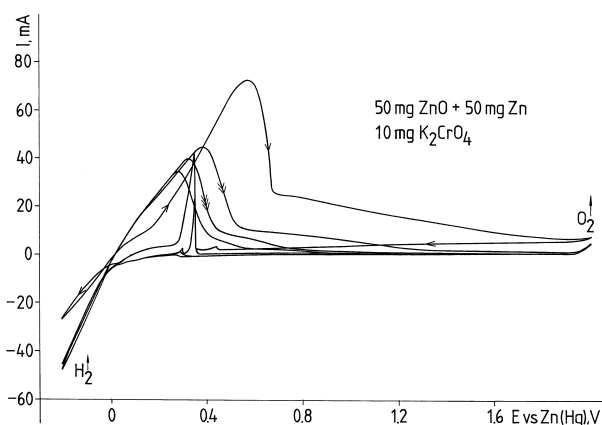


Fig. 2. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 10 wt.%  $K_2CrO_4$ . Potential range,  $-0.2$  to  $2.0$  V. Scan rate,  $1 \text{ mV s}^{-1}$ .

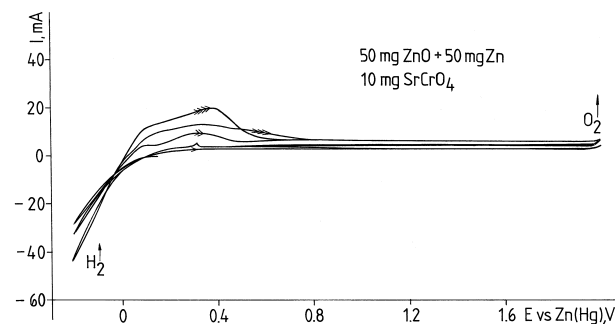


Fig. 3. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 10 wt.%  $SrCrO_4$ . Potential range,  $-0.2$  to  $2.0$  V. Scan rate,  $1 \text{ mV s}^{-1}$ .

out a various passivation effect depending on the kind and quantity of chromate additive. As mentioned above, in the case of potassium chromate, especially large decrease of the electrode charge is effected by 30% of additive which corresponds to the passivation degree of 62%. The following experiment showed that additional cathodic charge did not cause the reactivation. After several cycles the potential was stopped at the potential of reversion of  $-200$  mV until the charge of 50 C passed through the electrode. After such a treatment the charge increased only about 10 C and the electrode was passivated irreversibly. It seems therefore that 10% of  $K_2CrO_4$  is the optimum amount for maintaining the zinc electrode in active state. Figs. 2–4 represent voltammetric characteristics of the zinc electrodes with 10% of the following chromates: potassium, strontium and barium. Although the characteristics with  $K_2CrO_4$  and  $BaCrO_4$  differ from each other (especially for the first cycles), the transferred charges are comparable. Electrode with  $SrCrO_4$  behaves very peculiarly. In the first cycle it is almost inactive (11.6 C) but in the subsequent cycles electrode becomes gradually unblocked and finally gives 75.8 C.

Very specific properties of  $SrCrO_4$  encouraged us to devote more attention to this additive. For determination

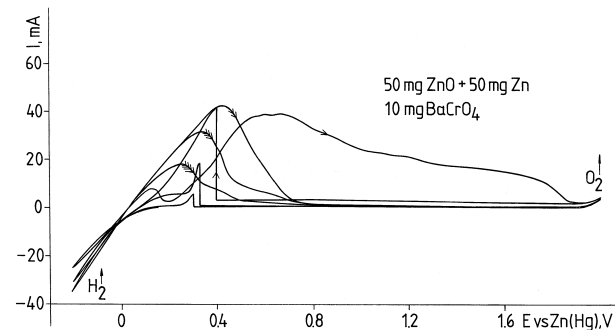


Fig. 4. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 10 wt.%  $BaCrO_4$ . Potential range,  $-0.2$  to  $2.0$  V. Scan rate,  $1 \text{ mV s}^{-1}$ .

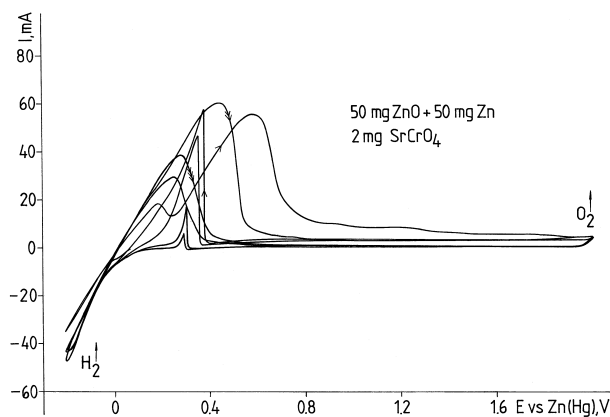


Fig. 5. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 2 wt.% SrCrO<sub>4</sub>. Potential range, –0.2 to 2.0 V. Scan rate, 1 mV s<sup>-1</sup>.

the minimum amount of additive capable of passivating the electrode, SrCrO<sub>4</sub> was inserted into electrode with increasing amount but every 1%. Figs. 5–7 depict electrochemical characteristics of these electrodes recorded during potentiodynamic runs. For the electrodes with above 4% of SrCrO<sub>4</sub> a distinct change in the character of voltammetric curves was observed. In the first cycle the electrode demonstrated inactivity. As seen in Fig. 7, for the zinc electrode admixed with 30% of SrCrO<sub>4</sub> the significant cathodic and anodic peak is observed. However, during the subsequent cycles it is not remarkable. It is noteworthy that for the electrode with more than 5% of SrCrO<sub>4</sub> the reactivation region with typical current oscillations almost disappears. This result is evidence for very efficient passivation effect of strontium chromate. It should be noticed that the current flows through the paths of a high electric resistivity after the electrode is passivated. The blocking of the pores in the zinc electrode by insoluble species produced in reaction with SrCrO<sub>4</sub> can also bring about the charge loss because some active material can loose electrical contact. For the practical application the amount of strontium chromate in secondary zinc electrode should not exceed 3–5%.

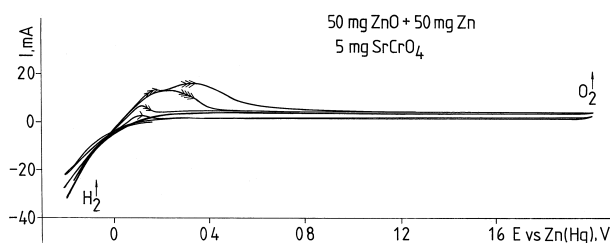


Fig. 6. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 5 wt.% SrCrO<sub>4</sub>. Potential range, –0.2 to 2.0 V. Scan rate, 1 mV s<sup>-1</sup>.

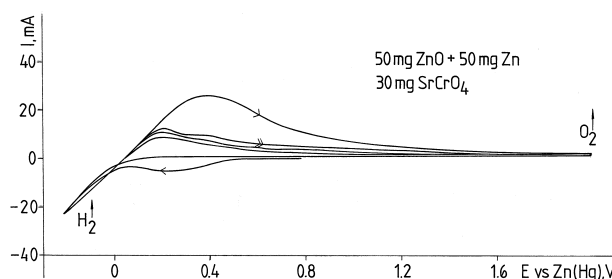


Fig. 7. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 30 wt.% SrCrO<sub>4</sub>. Potential range, –0.2 to 2.0 V. Scan rate, 1 mV s<sup>-1</sup>.

CrO<sub>3</sub>–GIC has been thought as useful material modifying the cyclic behaviour of zinc electrode. Contrary to CrO<sub>3</sub>–GICs prepared by the solvent method undergoing an instant deintercalation in water, deintercalation of the compounds prepared by both the dry and impregnation-dry method occurs very slowly even in acid and alkaline solutions of a high concentration [12,13,15]. Such a property is due to disordered structure of CrO<sub>3</sub>–GIC in which CrO<sub>3</sub> is caged in the graphite pockets and trapped in the crystallite boundaries originally present in the graphite host as well as formed during the intercalation process. On the other hand, during the purification of the product of intercalation the graphene layers of the formed CrO<sub>3</sub>–GIC are sealed at the periphery of flakes which gives rise to a high stability of the system on storage at ambient conditions. The structure as well as chemical and electrochemical properties of the system used in this work have been verified to remain unchanged even for a few years. Sample A2–W2 of moderate content of CrO<sub>3</sub> is composed of the graphite flakes significantly coarser as compared to the zinc particles.

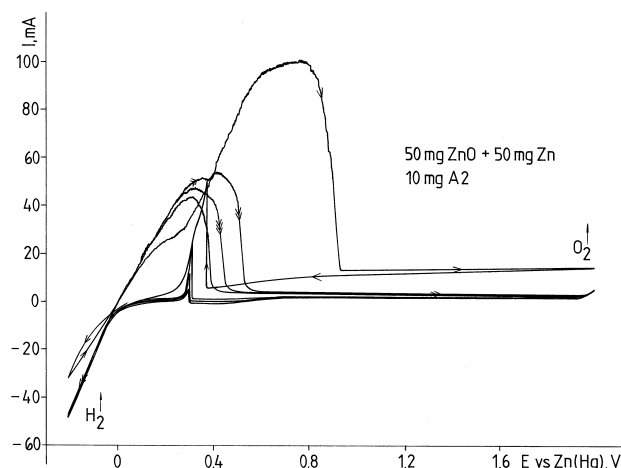


Fig. 8. Cyclic potentiodynamic curves recorded in 7 M KOH+0.6 M ZnO for Zn–ZnO electrode admixed with 10 wt.% flaky graphite (A2). Potential range, –0.2 to 2.0 V. Scan rate, 1 mV s<sup>-1</sup>.

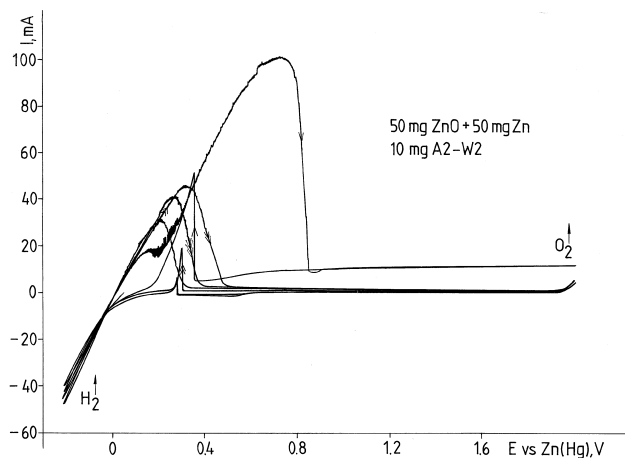


Fig. 9. Cyclic potentiodynamic curves recorded in 7 M KOH + 0.6 M ZnO for Zn–ZnO electrode admixed with 10 wt.%  $\text{CrO}_3$ –graphite system. Potential range,  $-0.2$  to  $2.0$  V. Scan rate,  $1 \text{ mV s}^{-1}$ .

As can be seen from Table 2, the charge drawn out all the electrodes admixed with the  $\text{CrO}_3$ –graphite system is lower than that of the original zinc electrode. This effect can be attributed to the passivation of zinc by  $\text{CrO}_3$  released from the additive. The potentiodynamic curves illustrated in Figs. 8 and 9 are consistent with this conclusion. Especially marked decrease of charge is noted for the electrode with 30% of additive. The charge for this electrode is comparable to the electrodes with 10% of  $\text{K}_2\text{CrO}_4$  and 1% of  $\text{SrCrO}_4$ . The comparison of the amount of Cr(VI) present in the electrodes admixed with the mentioned chromates and with sample A2–W2 allow to approach to more conclusive interpretation. The calculations show that, as compared to the 30% A2–W2 admixture, 1.4 times more and 7 times less chromium is present in the 10%  $\text{K}_2\text{CrO}_4$  and 1%  $\text{SrCrO}_4$  additive, respectively. This result is encouraging for further studies on the application of  $\text{CrO}_3$ –GICs as passivating additive to zinc electrode. The performance of  $\text{CrO}_3$ –GIC can simply be improved by using the compound containing more intercalate and composed of finer graphite flakes. In such a way, the mixture electrode will become more homogeneous and more chromium ions will be supplied to the zinc–graphite interface. Consequently, chromium ions would interact with the zinc surface more effectively and the electrical contact between the particles of electrode would be improved. The decrease in the electrical resistivity of the electrode is especially important for the rechargeable zinc anodes in which the passive layers of a high resistivity are formed during anodic process. It is worth to recall at this point that  $\text{CrO}_3$ –GIC of the desired properties has been prepared previously [13,14,16]. Its flakes are smaller than  $25 \mu\text{m}$  in diameter whereas the chromium content ( $\text{C}/\text{Cr} = 13.6$ ) is over four times higher than that of sample A2–W2. Such a compound is intended for further work.

#### 4. Conclusions

Additive of chromium compounds to the zinc electrode material caused a different passivation effect depending on the solubility of Cr compounds and availability of Cr ions to the Zn–electrolyte interface. Passivation of zinc material limited the dissolution of anodic products and allowed their retention in the interior of porous electrode. In such a way, the mechanism of zinc dissolution changed from the heterogeneous into solid state type and cyclic performance of zinc electrode was improved.

The most effective additive for passivation was potassium chromate but only with more than 10%. In the case of strontium chromate passivation could be better controlled. It was found that the passivation effect was depended on the cation of chromate used and on the size and morphology of chromate particles.

It was evidenced that  $\text{CrO}_3$ –graphite system added to the powder Zn electrode exhibited passivating properties. In the case of this additive the mechanism of passivation is based on a gradual exhaustion of the  $\text{CrO}_3$  intercalate from the lattice of intercalation compound to the electrolyte followed by hydrolysis at the Zn–graphite interface.

Application of chromium additives to Zn electrode material, with a controlled passivation effect, results in the limited zinc solubility and cycling improvement of accumulators with Zn anode.

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