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Comparative EIS study of a paste electrode containing zinc powder in neutral and near neutral solutions

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Abstract The corrosion and passivation of Zn powder particles dispersed in a paste electrode immersed in 0.5 M Na₂SO₄ and 5×10⁻³ M Na₂HPO₄ solutions were studied mainly by electrochemical impedance spectroscopy. The role played by diffusion in the mechanism of anodic oxidation of zinc powder particles has been shown. It was demonstrated that the anodic reaction of Zn powder in neutral or near neutral media involves at least two adsorbed intermediates. By simulating the porous structure of the electrode, some information about porous nature of zinc electrode could be extracted.

Keywords Zinc corrosion · Electrochemical impedance spectroscopy · Carbon paste electrode · Porous structure

Introduction

Owing to its use as a sacrificial anode, the corrosion of Zn in neutral media is of great interest, although the electrochemical behavior of a Zn electrode in neutral and near neutral solutions has not been extensively studied. Generally, most papers are dedicated to the behavior of a Zn anode in alkaline media [1, 2, 3, 4, 5] because of its employment in alkaline batteries. Hubbard and Shanahan [6] have studied a Zn electrode in NaHCO₃, Na₂CO₃, chloride and nitrate solutions by means of potential-time curves. They have found that the corrosion product in near neutral solutions is mainly zinc oxide containing small amounts of zinc hydroxide.

Using a Zn rotating disk electrode (RDE), Boto and Williams [7] have shown that in Na₂SO₄ solution, at pH 5.6–6.2, the overall corrosion reaction is diffusion controlled. Baugh [8] has determined the corrosion rates of Zn in NaClO₄, NaCl and Na₂SO₄ in the pH range 3.0–5.8. Studying a Zn electrode in sulfate solutions, Sziraki et al. [9] have found recently that the corrosion kinetics is determined by mass transport and migration properties of the film formed by passivation. However, in all previous studies the working electrode used has been a massive Zn electrode. The present paper deals with the electrochemical behavior of Zn powder particles dispersed in a carbon paste electrode which is immersed in 0.5 M Na₂SO₄ and 5×10⁻³ M Na₂HPO₄ neutral or near neutral solutions.

Experimental

Electrochemical measurements were performed at room temperature using a classical three-electrode system. The working electrode was a carbon paste electrode having the following composition (% weight): 42.8% Zn powder (Merck), 42.8% carbon powder (Merck) and 14.4% carbon paste (BASF). The size of the Zn powder particles ranged between 40 and 50 µm. The geometrical surface area of the working electrode was 0.125 cm². A saturated calomel electrode was used as reference electrode and a Pt foil was the counter electrode. The Na₂SO₄ and Na₂HPO₄ solutions were prepared from pure reagents (Panreac) and distilled water. Polarization and cyclic voltammetry measurements were performed using an EG&G PAR 263A potentiostat. For impedance data acquisition a PARC 5210 lock-in amplifier was used. The voltage amplitude of the sinusoidal signal was 10 mV, the frequency ranging from 10⁻² Hz to 10⁵ Hz. EIS results have been analyzed using the complex nonlinear least squares impedance fitting program LEVM, version 7.1, of MacDonald [10].

Results and discussion

The corrosion and passivation of Zn powder particles dispersed in a paste electrode in contact with either 0.5 M Na₂SO₄ solution (pH 6.8) or 5×10⁻³ M Na₂HPO₄ solution (pH 8.6) were investigated. The electrochemical

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impedance spectroscopy technique was mainly employed because it gives valuable information about the mechanism of electrochemical reactions. Cyclic voltammetry and linear polarization techniques were also used.

Electrochemical behavior of Zn particles contained in a paste electrode in 0.5 M Na₂SO₄ solution

The cyclic voltammogram presented in Fig. 1 shows the anodic oxidation peak of the Zn particles. The descending part of this peak can be ascribed to the passivation by oxide film formation on the Zn surface. However, because the amount of Zn powder particles on the electrode surface is limited and probably is not supplied from the bulk of the electrode, the extent of the Zn diminishing reaction (corrosion reaction) should also be taken into account.

More information about the mechanism of the oxidation reaction can be obtained from the anodic linear polarization curve of the carbon paste electrode containing Zn powder particles which was immersed in 0.5 M Na₂SO₄. The curve, shown in Fig. 2, presents two linear regions instead of one linear region. The presence of these regions on the polarization curve was interpreted by two parallel ways occurring in the oxidation process of Zn. These parallel ways in the oxidation mechanism involve adsorbed intermediates species Zn^I_{ads} and Zn^{II}_{ads}, as pointed out by Sziraki et al. [9].

The use of electrochemical impedance spectroscopy helps us in clarifying the mechanism of the anodic reaction. Figure 3 shows the electrochemical impedance spectra in a Nyquist plot for two values of the polarization potentials: -1.05 V, close to the open circuit potential of a zinc paste electrode in 0.5 M Na₂SO₄, and -0.8 V, where the passive oxide film is already formed. One can notice the depressed semicircles in the Nyquist complex plot, which are characteristic of materials with

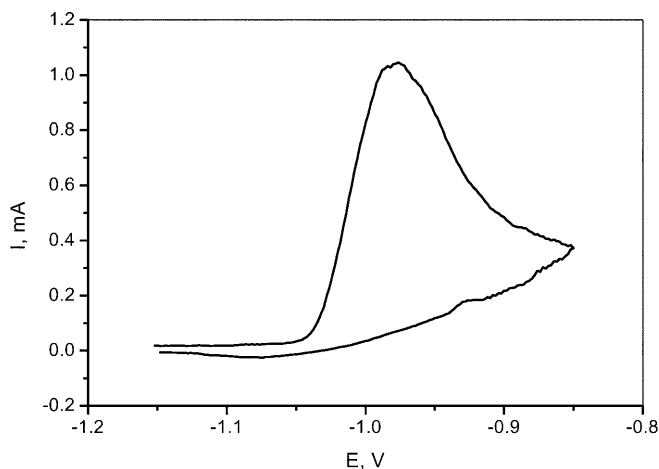


Fig. 1 Cyclic voltammogram of carbon paste electrode containing zinc powder particles, immersed in a 0.5 M Na₂SO₄ solution; scan rate 0.4 mV/s

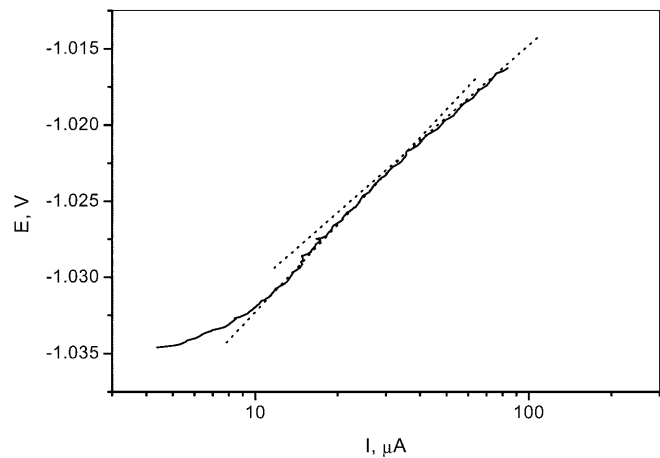


Fig. 2 Linear polarization of Zn powder particles embedded in a carbon paste in contact with 0.5 M Na₂SO₄ solution

various degrees of surface roughness, as well as the Warburg-type impedance at low frequencies. These data suggest that the rate-determining step in the corrosion mechanism of Zn particles dispersed in a carbon paste electrode is diffusion, in agreement with the work of Boto [7] on a Zn rod electrode.

In the fitting of impedance data, a constant phase element (distributed element in the LEVM program) was used instead of a simple capacitor. Its impedance response, Z , is expressed as:

$$Z = [Y(j\omega)^n]^{-1} \quad (1)$$

where Y acts as a capacitance when $n=1$, ω is the angular frequency of the a.c. signal and $j=\sqrt{-1}$.

The use of a constant phase element is appropriate for the study of electrodes with different degrees of surface roughness, either showing physical non-uniformity or a non-uniform distribution of the surface

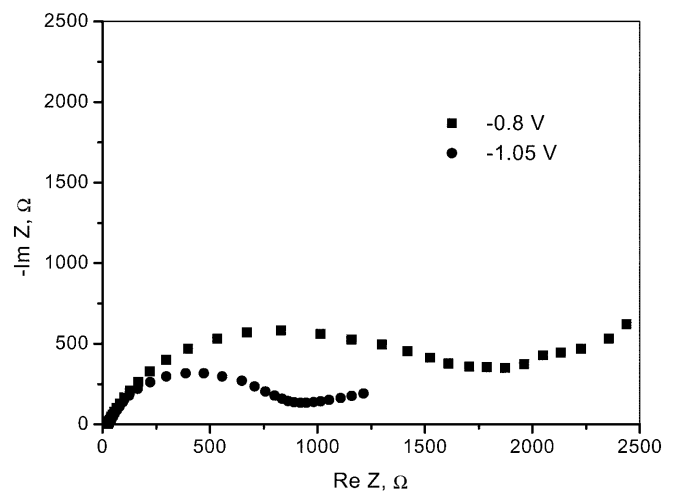


Fig. 3 Nyquist diagram of a paste electrode containing Zn powder in 0.5 M Na₂SO₄ at -1.05 V and -0.8 V

reaction [11, 12]. When the value of parameter n becomes 1, then the distributed element is a pure capacitor; if n is 0.5 the distributed element is a pure Warburg impedance; if n is zero the distributed element is a pure resistance. The proposed fitting circuits are presented in Fig. 4; the fitting result, in a Bode diagram, for Zn contained in a paste electrode at -1.05 V and -0.8 V is shown in Fig. 5. In the proposed fitting, circuits DE_1 and DE_2 act as a pseudo-capacitor while DE_3 acts as a pseudo-Warburg impedance, because their n values tend to 1 and 0.5, respectively. The values of the parameters from simulations of the impedance spectra are listed in Table 1, together with the mean percentage deviation of real and imaginary parts of the impedance. The two high values of the mean percentage deviation from Table 1 are due to the disagreement between the calculated and experimental impedance of the few points at high or low frequencies (Fig. 4b and Fig. 7, respectively).

In neutral or near neutral solutions, even at the open circuit potential, a film is formed spontaneously on the Zn particle surface so that a diffusional process will accompany Zn dissolution. This can be easily seen from the shape of the Nyquist diagram at low frequencies in Fig. 3. The resultant oxide layer is thick enough to impede both diffusion of hydroxide ions towards the electrode surface and the diffusion of reaction products (e.g. Zn^{2+} ions) towards the bulk of the solution, leading to a diffusion-controlled mechanism. Taking into account the above information, circuit (a) from Fig. 4 has been found to give the best results for the impedance spectra at -1.05 V. The first time constant (DE_1-R_1) is attributed to the faradaic charge transfer process, while the second one (DE_2-R_2) corresponds to the adsorbed species that appear in the oxidation mechanism. At -0.8 V the fitting circuit represents the single layer model with roughness factor and Warburg impedance [the (b) circuit from Fig. 4]. The difference between the phase angle at -1.05 V and -0.8 V electrode potentials (Bode diagrams from Fig. 5) can be related to the barrier properties of the anodic film formed on the metallic surface. The oxide film is thicker at -1.05 V and diffusion is the limiting step in the oxidation mechanism. In both cases the oxide film has a porous structure.

Fig. 4 Equivalent circuits used to fit the impedance spectra (R_i , resistors; DE_i , distributed elements; L , inductance): **a** the model used for fitting the impedance spectra of Zn particles in 0.5 M Na_2SO_4 at -1.05 V; **b** the model used for fitting the impedance spectra of Zn in Na_2SO_4 (0.5 M) at -0.8 V and Zn in Na_2HPO_4 (5×10^{-3} M) at -0.75 V; **c** the model used for fitting the impedance spectra of Zn in Na_2HPO_4 (5×10^{-3} M) at -0.5 V

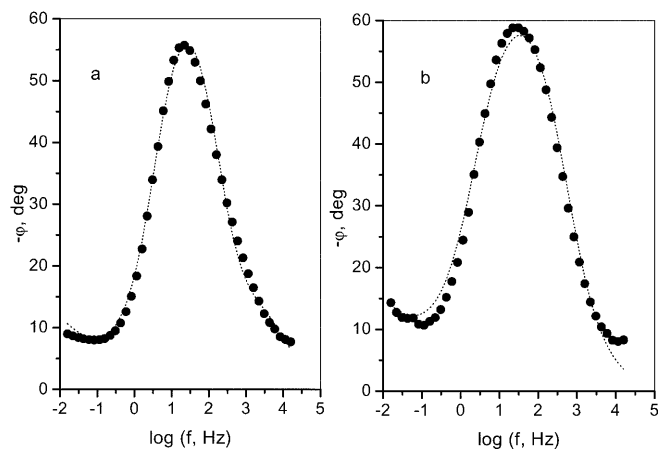
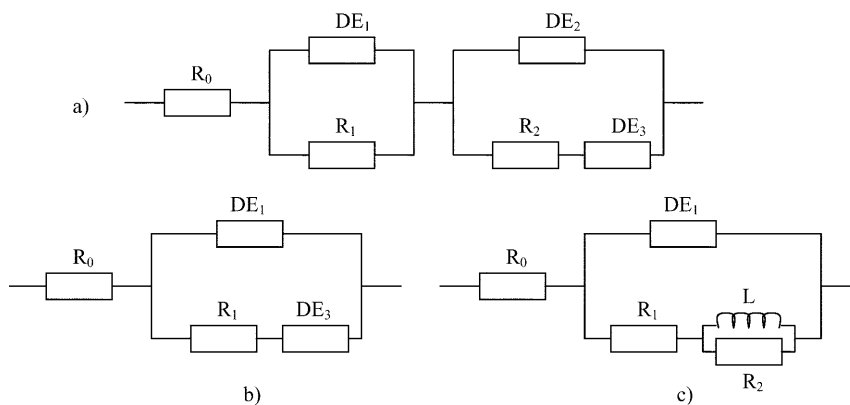


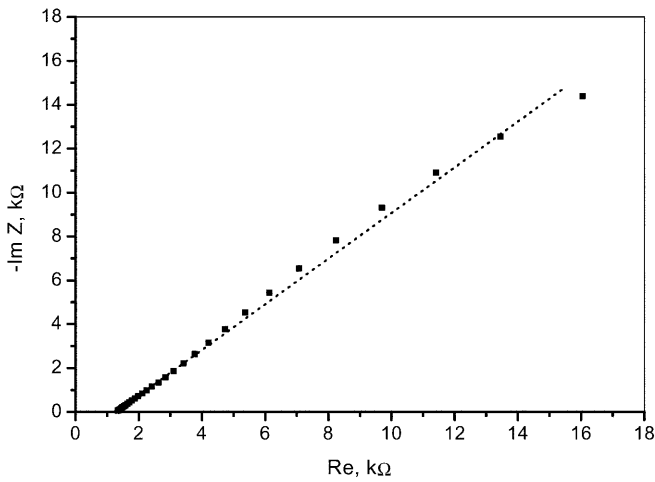
Fig. 5 Bode plots for a carbon paste electrode containing Zn powder particles, immersed in 0.5 M Na_2SO_4 at **a** -1.05 V and **b** -0.8 V. The dotted line represents the fitted circuit for the model shown in Fig. 4a and for the model shown in Fig. 4b, respectively

Electrochemical behavior of Zn particles contained in a paste electrode in 5×10^{-3} M Na_2HPO_4 solution

One of the advantages of electrochemical impedance spectroscopy is that it can be used to study the electrode processes in very dilute electrolytes such as 5×10^{-3} M Na_2HPO_4 solution. From the recorded Tafel plot (not shown here), two polarization potentials were chosen to perform the impedance spectra: -0.75 V in the cathodic region (hydrogen evolution) and -0.5 V, corresponding to the anodic branch of the curve. The Nyquist impedance representation for a paste electrode containing embedded Zn powder particles, polarized at -0.75 V (Fig. 6), shows a pronounced diffusive component having the value of $n=0.518$ (see Table 1). From impedance spectra at -0.5 V (Fig. 7) we can suppose that the anodic reaction of Zn powder particles dispersed in the paste electrode involves at least two adsorbed intermediates. It is worth mentioning that in such a dilute solution the oxide layer does not act any longer as a rate-limiting parameter, so that it is possible to reveal the presence of adsorbed species by the inductive loop in the Nyquist diagram.

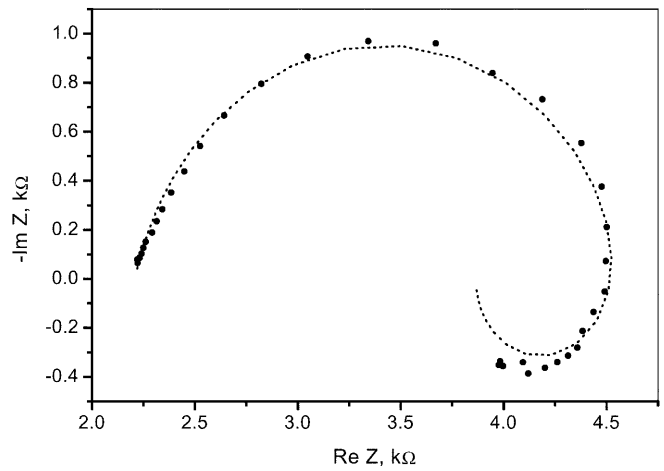
Table 1 Values of the parameters used in the simulation of the impedance spectra

Solution		0.5 M Na ₂ SO ₄		5×10 ⁻³ M Na ₂ HPO ₄	
Potential (V)		-1.05	-0.8	-0.75	-0.5
R ₀ (Ω)		20.9 ± 0.72	23 ± 0.87	1160 ± 9.23	2236 ± 11.12
R ₁ (Ω)		9.94 ± 0.68	1491 ± 52.67	134 ± 5.1	1534 ± 55.89
R ₂ (Ω)		779 ± 23.62	—	—	771 ± 50.24
DE ₁	Y (Ω s ⁻ⁿ)	(6.021 ± 0.831)×10 ⁻⁵	(8.13 ± 0.94)×10 ⁻⁵	(0.868 ± 0.085)×10 ⁻⁶	(20.4 ± 2.85)×10 ⁻⁶
	n	0.764 ± 0.043	0.779 ± 0.087	0.753 ± 0.016	0.818 ± 0.013
DE ₂	Y (Ω s ⁻ⁿ)	(8.779 ± 0.549)×10 ⁻⁵	—	—	—
	n	0.845 ± 0.018	—	—	—
DE ₃	Y (Ω s ⁻ⁿ)	(7879 ± 484)×10 ⁻⁶	(2.73 ± 0.157)×10 ⁻³	(159.2 ± 14.27)×10 ⁻⁶	—
	n	0.4 ± 0.037	0.38 ± 0.034	0.512 ± 0.049	—
L (H)		—	—	—	720 ± 42.17
Re deviation (%)		3.99	5.67	1.34	2.15
Im deviation (%)		4.96	13.03	2.14	25.26

**Fig. 6** Impedance plot of Zn particles dispersed in a paste electrode for 5×10⁻³ M Na₂HPO₄ solution at -0.75 V. The *dotted line* represents the fitted model for the circuit in Fig. 4b

A possible source of errors in the electrochemical behavior of the paste electrode containing metallic particles could arise from the oil content of the carbon paste. It could be possible that Zn powder particles (and generally the electroactive particles) are surrounded by the oil. Spreading the oil on the surface of the powder can affect the electrochemical behavior of electroactive particles, modifying the value of double layer capacity and also influencing the charge transfer reactions. For this reason, special caution should be taken with carbon paste, although the oil is generally considered completely inert in the chemical sense and also in a faradaic electrochemical sense. However, in the present work we believe that the oil from the carbon paste had no influence because of two reasons: (1) the content of the carbon paste is less than 15%, so the oil content from the paste should be less, and (2) the impedance diagrams and cyclic voltammograms seem not to be affected by a capacitive response or ohmic drop which are characteristic for oil.

In order to check the internal consistency of the impedance data set, the Kramers-Kronig transforms

**Fig. 7** Impedance plot of Zn particles dispersed in a paste electrode in 5×10⁻³ M Na₂HPO₄ solution at -0.5 V. The *dotted line* represents the fitted model with the circuit in Fig. 4c

should be useful. As was shown previously [12], these transforms can be applied successfully if the following four conditions are fulfilled:

1. The response of the system is due only to the perturbation applied.
2. The impedance is independent of the magnitude of the perturbation.
3. The system must be stable, returning to its original state after the perturbation has been removed.
4. The impedance must have finite values at $\omega \rightarrow 0$ and $\omega \rightarrow \infty$ frequencies and must be a continuous and finite-valued function at all intermediate frequencies.

In the present work the real part of impedance data was used in order to calculate the imaginary part of the impedance; the polarization resistance was also estimated. The corresponding equations are:

$$Z''(\omega) = -\frac{2\omega}{\pi} \int_0^{\omega} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx \quad (2)$$

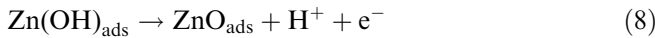
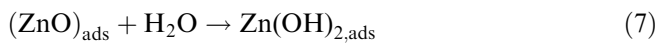
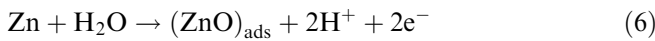
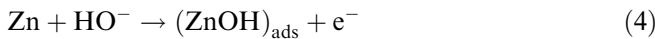
and:

$$R_p = \frac{2}{\pi} \int_0^{\infty} \frac{Z''(x)}{x} dx \approx \frac{2}{\pi} \int_{x_{\min}}^{x_{\max}} \frac{Z''(x)}{x} dx \quad (3)$$

where Z' and Z'' are the real and imaginary components of the impedance, respectively; both ω and x are a.c. frequencies and R_p is the polarization resistance.

As can be seen from Fig. 8, the impedance data set at -0.75 V polarization potential were not validated by Kramers-Kronig transforms because the condition (4) was not fulfilled. The transforms cannot be applied if a Warburg component appears in the impedance spectra. On the contrary, because the Warburg component was not present, the impedance data at -0.5 V were validated by Kramers-Kronig transforms, except for low-frequency data which were affected by the transformations occurring at longer acquisition times. However, even so, the inductive character of the impedance in this low-frequency range was validated. By applying Eq. 3 the estimated value of the polarization resistance was found to be 1341Ω , a value which is in fairly good agreement with that obtained by fitting the experimental impedance spectra (1534Ω in Table 1).

Taking into account the above results, the proposed reaction mechanism for Zn anodization has a reaction scheme according to Fig. 9, where the suggested processes are:



One may note that the overall process of zinc anodic oxidation going to the final reaction product, $\text{Zn}(\text{OH})_{2,\text{ads}}$, takes place by two parallel pathways, each one involving an adsorbed intermediate, covering concurrently the surface of the electrode. Because of a small concentration of hydroxide ions in the neutral or near neutral media used, it is expected that the adsorbed $(\text{ZnO})_{\text{ads}}$ pathway is to be preferred instead of the $(\text{ZnOH})_{\text{ads}}$ pathway.

Porous structure modeling of the paste electrode containing Zn powder particles

A model proposed by Gassa et al. [13] has been used to simulate the impedance behavior of a porous paste electrode containing embedded zinc powder particles in contact with 5×10^{-3} M Na_2HPO_4 solution. In this model

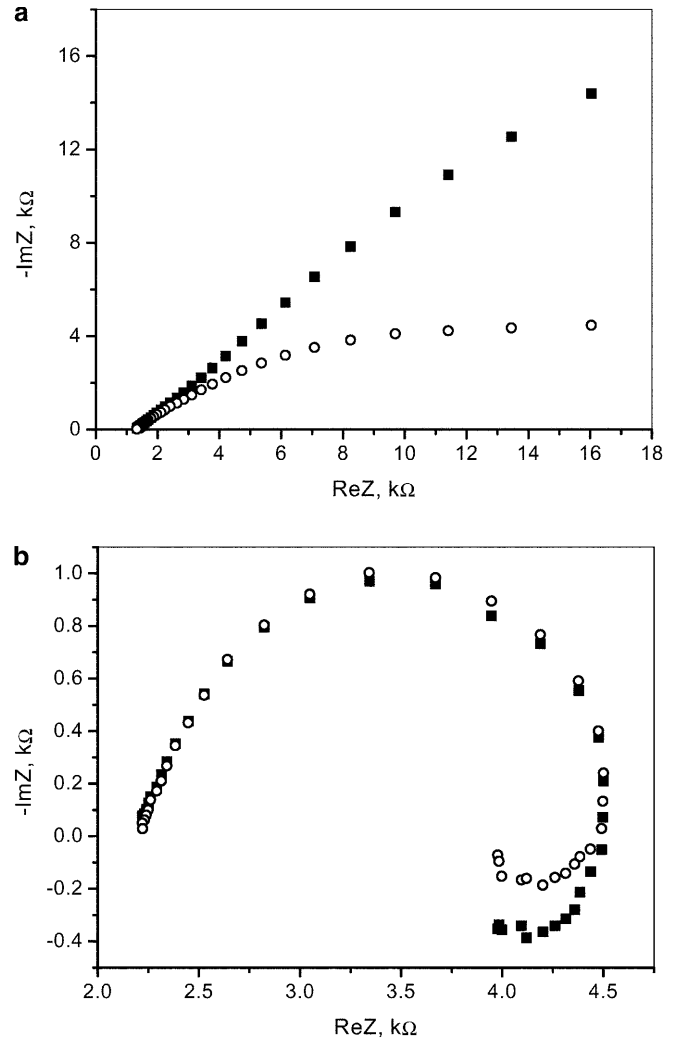


Fig. 8 Kramers-Kronig transforms for a paste electrode containing Zn particles in 5×10^{-3} M Na_2HPO_4 solution at two electrode potentials: **a** -0.75 V and **b** -0.5 V; ■ experimental data, ○ calculated data

the impedance expression for a cylindrical pore, Z_p , is given by:

$$Z_p(j\omega) = \frac{1}{\pi r} \sqrt{\frac{\rho Z_0(j\omega)}{2r}} \coth \sqrt{\frac{2\rho l^2}{r Z_0(j\omega)}} \quad (9)$$

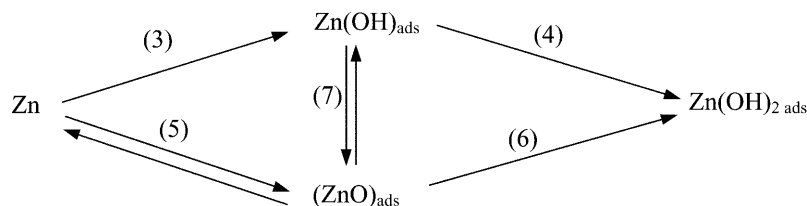
with r the pore radius, l the length of a pore, and ρ the specific resistivity of the electrolyte in the pores. It was denoted by $Z_0(j\omega)$, the specific impedance per unit area of a cylindrical pore.

Because of the non-homogenous nature of the carbon paste electrode containing Zn powder particles, its specific impedance will be expressed as:

$$Z_0(j\omega) = \frac{R_t}{1 + (j\omega R_t C_{dl})^\alpha} \quad (10)$$

where R_t and C_{dl} represent the charge transfer resistance and double layer capacity, respectively, and α ranges between 0 and 1.

Fig. 9 Proposed mechanism of Zn powder electrochemical dissolution in neutral and near neutral media



The overall impedance for a porous electrode having n pores per unit surface area is then:

$$Z(j\omega) = R_{\Omega} + Z_p(j\omega)/n \quad (11)$$

Equation 11 can be rearranged in a simpler form, necessary to perform the simulation. Thus, one can write:

$$Z = R_{\Omega} + R_{\Omega,p} \sqrt{\frac{A}{1 + (j\omega AB)^{\alpha}}} \coth \sqrt{\frac{1 + (j\omega AB)^{\alpha}}{A}} \quad (12)$$

where $A = \frac{rR_l}{2\rho l^2}$, $B = \frac{2\rho l^2 C_{dl}}{r}$ and $R_{\Omega,p} = \frac{\rho l}{n\pi r}$. By adjusting the values of the A , B , $R_{\Omega,p}$ and α parameters, the following set was found to give the minimum errors for the impedance data shown in Fig. 7: $A = 31.6 \pm 3.4 \text{ m}^{-2}$, $B = 19.5 \pm 2.1 \text{ s}$, $R_{\Omega,p} = (3 \pm 0.3154) \times 10^3 \Omega \text{ m}^2$ and $\alpha = 0.1 \pm 5 \times 10^{-4}$. We believe that the resultant parameters are reliable, taking into account the order of magnitude for the physical constants involved in each parameter. The simulating results are in very good agreement with the experimental data (Fig. 10), showing the validity of the pore model in the case of the carbon paste electrode containing Zn particles.

Some structural parameters can be extracted from the above estimated constants. Thus, replacing in the formula of the A constant the value for R_l determined by modeling (see Table 1), one can obtain for the ratio $\frac{r}{\rho l^2}$ a value of 0.47Ω . Therefore, from the expression for the B constant, a double layer capacity of about 4.6 F/m^2 is obtained. Such a high value for the double layer capacity (one order of magnitude higher than usually) can be explained by the large surface area of a carbon paste electrode containing metal particles. Unfortunately, the characteristic parameters for pores (radius and length) cannot be determined separately. Nevertheless, assuming for the solution resistivity in pores a similar value as for the bulk resistivity (about $17 \Omega \text{ m}$ for $5 \times 10^{-3} \text{ M Na}_2\text{HPO}_4$ solution), a quite reasonable value of 8 m^{-1} is obtained for the $\frac{r}{l^2}$ term. Of course, the pores from the carbon paste electrode will not have a cylindrical shape. That is why r and l will not have the above significances but rather the mean dimensions between the Zn-Zn or Zn-C particles.

Conclusions

Electrochemical impedance spectroscopy has proven to be a valuable technique for investigation of the electrochemical behavior of zinc powder particles dispersed in a

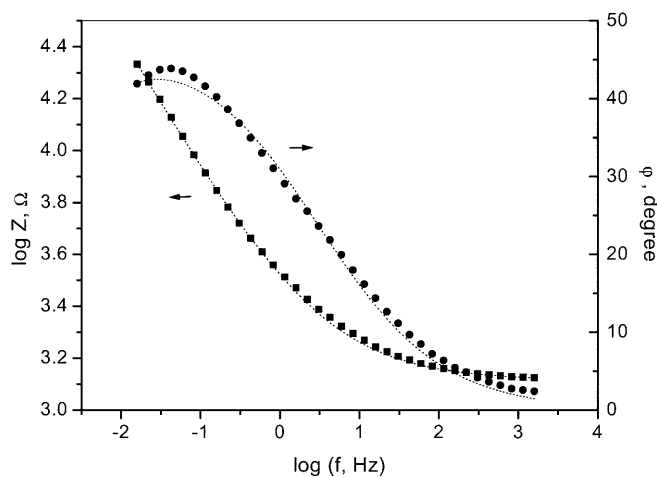


Fig. 10 Bode diagram of a pore model simulation for a paste electrode containing Zn particles in contact with $5 \times 10^{-3} \text{ M Na}_2\text{HPO}_4$ at -0.75 V

carbon paste electrode in contact with Na_2SO_4 and Na_2HPO_4 solutions. The Warburg-type impedance at low frequencies from impedance spectra for Na_2SO_4 solution allowed us to suppose the occurrence of a passive film on zinc powder particles situated on the electrode surface, which impedes the diffusion and acts as a barrier. In Na_2HPO_4 solution the impedance spectrum changes dramatically, showing a different impedance behavior. The inductive behavior observed in the low-frequency domain for Na_2HPO_4 solution indicates that at least two adsorbed species are involved in the mechanism of Zn oxidation. On the basis of the experimental results, a model was proposed for anodic oxidation of zinc powder particles in the above neutral and near neutral media. It was also shown that the porous structure of paste electrodes can be successfully simulated and some parameters of the pores could be determined from the simulation.

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