

Metal–electrolyte interface interaction on a negative electrochemical device

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Abstract

The negative electrochemical device (NED) is a surface system found in many polycrystalline metal alloy microstructures. NED consists of a multiple electrode galvanic micro-cell with a heterogeneous distribution. Some difficulties for performing experimental work at the microscopic scale and raw interest on technological applications have made NED not much studied in the past, but future nanotechnological applications are making it more interesting to study. The loss of matter on the metal–electrolyte interface due to redox reactions is assessed. Redox reactions have a natural direction to occur, determined by the chemical potential of reactants. Once the reactions occur, there is no way of turning back the oxide species to their original reduced form, meaning that an irreversible entropy has been produced into the system. A new array of the multicomponent Gibbs ensemble is applied and a Young–Laplace equation is proposed for dealing with surface tension. Finally, the mass and entropy interactions are described by the corresponding balance equations.

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1. Introduction

Electrochemical methods describe galvanic action on a metallic surface by considering steady state reversible redox reactions occurring in the metal–electrolyte interface [1]. For accounting the amount of metal dissolved in unit time, a kinetic factor is applied when the system is out of equilibrium. The interchange current density (i_0) takes account of electron flux generated during the oxidation and equating the amount of electrons needed for reduction on each metal–electrolyte interface; the greater i_0 , the easier charge transfer [2]. Nevertheless, when a metal alloy is corroded under realistic conditions, it losses matter on the interface in contact with the environment due to redox reactions between different ionic species dissolved in the electrolyte solution. Redox reactions occur with a natural direction determined by the chemical potential of reactants. This means that irreversible entropy production has occurred and part of the metal has been irreversibly dissolved. The oxide species appear next to the cathode areas and the matter exchange modifies the

stress resisting structure on the material because of a loss of mass.

2. The system

The negative electrochemical device (NED) in a polycrystalline metal alloy can be regarded as a unitary surface element of an open system, consisting on multiple heterogeneously distributed electrodes. As long as the metal structure grains are next to each other, the micro-cell electrodes in such a device are in short circuit. The electrolyte is any electrically conductive solvent containing ionic species and not fulfilling the Henry's Law. With all these elements, a NED has the special feature of being a substance destroyer and an energy consumer device [3].

In order to find a relationship between the electrochemical and mechanical forces occurring on the surface of a polycrystalline metal in electrochemical conditions, the Gibbs ensemble is proposed [4]. The representative volume element is conventionally established. It has to be mesoscopically small enough to be a point but microscopically big enough to represent the mean properties of the material. The metal alloy microstructure consists on phases (α) and (γ), representing two different types of grains. Phase (ι) is the electrolyte and phase (κ) is a virtual

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Nomenclature

dA	surface element differential area
dn_i	change in mass of component i
i_0	interchange current density
J_j	are reaction fluxes
J_s	entropy flux defined by Eq. (17)
M_i	molecular mass of component i
NED	negative electrochemical device
P	pressure
S	entropy
S_ψ	entropy production due to non-equilibrium processes per unit volume and time
T	temperature
U	internal energy
V	volume
W_S	surface strain work due to the metal–electrolyte interface interaction on the negative electrochemical device

Greek letters

(α)	anode phase
(γ)	cathode phase
ζ_i	rate of transformation of component i per unit volume and time, due to the chemical reactions on which i is participating
(l)	electrolyte phase
μ_i	chemical potentials
v_i	velocity of the component i
ξ_j	state of reaction j
ρ_i	mass density of the component i
σ	surface tension
(σ)	virtual interface for the Gibbs ensemble
ν_{ji}	stoichiometric coefficients of reaction j
<i>Note:</i>	Capital letters like A , S or V refer to the extensive magnitudes of properties, while lower case letters refer to their corresponding intensive magnitudes.

interface that deals with energy, entropy and composition differences between the metal and the electrolyte. The ensemble of (α) , (γ) , (l) and (κ) , will be a representative volume element of the actual (NED) system (see Fig. 1). Throughout this paper and inside the equations, the different phases or subsystems are indicated inside parentheses.

3. The interface interaction

We can start our analysis by applying the first principle of thermodynamics, making the internal energy states of our system dependent on entropy, volume and components: $U = U(S, V, n_1, \dots, n_C)$. When we differentiate the internal energy function we get [4]:

$$dU = T dS - P dV + \sum_i^C \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} dn_i \quad (1)$$

Here, the chemical potentials μ_i are defined as

$$\mu_i = \sum_i^C \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} \quad (2)$$

For NED to be representative, we take its volume to remain constant, so that its extensive properties shall depend on the limiting borders. Once the limits are fixed, the volume term in Eq. (1) vanishes and the internal energy variation of the system $dU^{(NED)}$ results from the sum of two terms: the energy variation due to the total entropy $T dS$ and the energy variation due to chemical reactions $\mu_i dn_i$. That is, the chemical potential μ_i times the change in the amount of mass dn_i :

$$dU^{(NED)} = T dS^{(NED)} + \sum_i^C \mu_i dn_i^{(NED)} \quad (3)$$

Subsystems (α) , (γ) , and (l) are representative volume elements with the same properties of their corresponding crystals on the metal and their volumes can change with the only restriction that the total volume of the ensemble remains constant. The internal energies for (α) , (γ) , and (l) are

$$dU^{(\alpha)} = T dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} + \sum_i^C \mu_i dn_i^{(\alpha)} \quad (4)$$

$$dU^{(\gamma)} = T dS^{(\gamma)} - P^{(\gamma)} dV^{(\gamma)} + \sum_i^C \mu_i dn_i^{(\gamma)} \quad (5)$$

$$dU^{(l)} = T dS^{(l)} - P^{(l)} dV^{(l)} + \sum_i^C \mu_i dn_i^{(l)} \quad (6)$$

Subsystem (κ) is a virtual interface surface that takes account of differences between (l) and $(\alpha) + (\gamma)$. It has no components, no volume and is subjected to surface strain work σdA , where σ is the surface tension and dA is the change of area. The internal energy for (κ) is

$$dU^{(\kappa)} = T dS^{(\kappa)} + \sigma dA \quad (7)$$

An explicit form of the Young–Laplace equation for NED is obtained by Eq. (3) with the ensemble (4) + (5) + (6) + (7) and

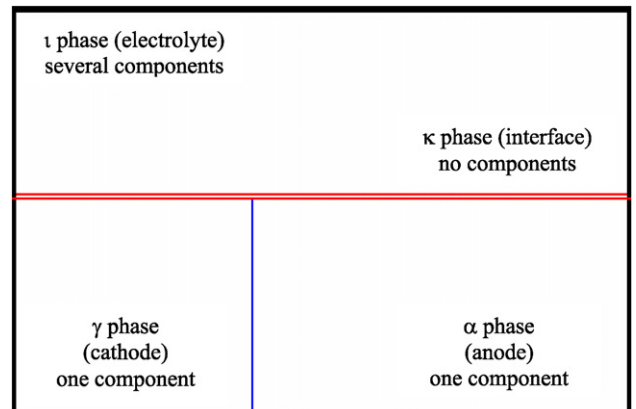


Fig. 1. The negative electrochemical device (NED).

solving for surface strain work (σdA) required on the interface for NED's volume to remain constant, we get:

$$\sigma dA = P^{(\alpha)} dV^{(\alpha)} + P^{(\gamma)} dV^{(\gamma)} + P^{(l)} dV^{(l)} \quad (8)$$

In order to find the mass interaction, we can apply the continuity equation, including the mass flux of component i by effect of diffusion $\rho_i \mathbf{v}_i$ and the mass flux due to chemical reactions [4], given that ρ_i is the mass density of the component i and \mathbf{v}_i is its velocity:

$$\frac{d\rho_i}{dt} = -\text{div}(\rho_i \mathbf{v}_i) + \zeta_i \quad (9)$$

The term ζ_i stands for the mass of component i which is transformed per unit volume and time, due to the chemical reactions on which i is participating:

$$\zeta_i = M_i \sum_{j=1}^r \nu_{ji} \mathbf{J}_j \quad (10)$$

Here, M_i is the molecular mass of component i , ν_{ji} the stoichiometric coefficients of reaction j and \mathbf{J}_j are the reaction fluxes, defined by the rate of j reaction's state (ξ_j/dt), according to the following definition [4]:

$$\mathbf{J}_j = \frac{1}{V} \left(\frac{d\xi_j}{dt} \right) \quad (11)$$

By means of the mass conservation principle, NED's mass remains constant: $d\rho^{(\text{NED})}/dt = 0$. Each type of grain on the metal structure consists of only one component and the electrolyte consists of several C components. Subsystem (γ) is a metastable cathode phase electrode and participates as a source of electrons to (l). Subsystem (κ), is a virtual surface with no volume. It has no mass and it does not contribute to mass exchanges into the system. Subsystem (l), the electrolyte, can have many components, each one participating on several possible reactions. Chemical reactions are held inside the electrolyte. The rates of transformation for each component i per unit volume due to the chemical reactions j , are calculated according to Eq. (10).

In order to find the continuity equations, we shall consider a diffusion component passing from (α), through (κ) and then to (l). The continuity equations for our system with two reactions ($j=1, 2$), are

$$\frac{d\rho_1}{dt} = -\text{div}(\rho_1 \mathbf{v}_1) + M_1 \nu_{11} \mathbf{J}_1 \quad (12)$$

$$\frac{d\rho_2}{dt} = -\text{div}(\rho_2 \mathbf{v}_2) + M_2 \nu_{12} \mathbf{J}_1 \quad (13)$$

$$\frac{d\rho_3}{dt} = -\text{div}(\rho_3 \mathbf{v}_3) + M_3 [\nu_{13} \mathbf{J}_1 + \nu_{23} \mathbf{J}_2] \quad (14)$$

$$\frac{d\rho_C}{dt} = -\text{div}(\rho_C \mathbf{v}_C) + M_C [\nu_{1C} \mathbf{J}_1 + \nu_{2C} \mathbf{J}_2] \quad (15)$$

For this case, between (14) and (15) we can have as many equations as the C components involved in describing the chemistry in the electrolyte.

The local equilibrium approach for irreversible processes states that the equilibrium equations are satisfied in small enough

elements of the system, even when the entire unit is out of equilibrium. Then, it is possible to use the Gibbs equation and solve it for the entropy. The general form of the entropy balance equation is

$$\rho \frac{ds}{dt} = -\text{div} \mathbf{J}_s + S_\psi \quad (16)$$

Being S_ψ the entropy production due to non-equilibrium processes per unit volume and time, and \mathbf{J}_s the entropy flux defined by

$$\mathbf{J}_s = \frac{1}{T} \left(\mathbf{J}_q - \sum_{i=1}^C \mu_i \mathbf{J}_i \right) \quad (17)$$

Applying (16) for (α) and (γ), the entropy balance equations are

$$\frac{ds^{(\alpha)}}{dt} = -\frac{1}{\rho^{(\alpha)}} [\text{div} \mathbf{J}_s^{(\alpha)} - S_\psi^{(\alpha)}] \quad (18)$$

$$\frac{ds^{(\gamma)}}{dt} = -\frac{1}{\rho^{(\gamma)}} [\text{div} \mathbf{J}_s^{(\gamma)} - S_\psi^{(\gamma)}] \quad (19)$$

Subsystem (κ) takes account of the entropy differences between (l) and the ensemble of (α) + (γ). We can apply (7) and solve for $ds^{(\kappa)}$ with respect to time:

$$\frac{ds^{(\kappa)}}{dt} = \frac{1}{T} \left[\frac{du^{(\kappa)}}{dt} - \sigma \frac{dA}{dt} \right] \quad (20)$$

For subsystem (l) the lagrangian equation is

$$\frac{ds^{(l)}}{dt} = -\frac{1}{\rho^{(l)}} [\text{div} \mathbf{J}_s^{(l)} - S_\psi^{(l)}] \quad (21)$$

Finally, the ensemble of entropy is

$$\begin{aligned} \frac{ds^{(\text{NED})}}{dt} = & -\frac{1}{\rho^{(\alpha)}} [\text{div} \mathbf{J}_s^{(\alpha)} - S_\psi^{(\alpha)}] - \frac{1}{\rho^{(\gamma)}} [\text{div} \mathbf{J}_s^{(\gamma)} - S_\psi^{(\gamma)}] \\ & + \frac{1}{T} \left[\frac{du^{(\kappa)}}{dt} - \sigma \frac{dA}{dt} \right] - \frac{1}{\rho^{(l)}} [\text{div} \mathbf{J}_s^{(l)} - S_\psi^{(l)}] \end{aligned} \quad (22)$$

Eq. (22) is an intensive expression of the entropy production rate which includes the electrochemical and mechanical forces relationship occurring on the surface of a polycrystalline metal. Important mechanical effects at low temperature and large surface tension can be predicted. Temperature exerts a positive but inverse influence on the entropy production rate, causing the system to increase its grades of freedom when it lows down, while surface tension exerts a negative direct influence, making the system to produce less entropy with respect to time when surface tension increases. If we wish the entropy production rate to be zero, we can solve (22) for the surface strain work ($W_S = \sigma dA$) and integrating when regarding σ constant over the surface to

obtain:

$$\begin{aligned}
 W_s = & U^{(\kappa)} - \frac{T}{\rho^{(\alpha)}} \int [\text{div } \mathbf{J}_s^{(\alpha)} - S_{\psi}^{(\alpha)}] dt \\
 & - \frac{T}{\rho^{(\gamma)}} \int [\text{div } \mathbf{J}_s^{(\gamma)} - S_{\psi}^{(\gamma)}] dt \\
 & - \frac{1}{\rho^{(\iota)}} \int [\text{div } \mathbf{J}_s^{(\iota)} - S_{\psi}^{(\iota)}] dt
 \end{aligned} \quad (23)$$

Eq. (23) stands for the surface strain work required to have no entropy production rate on the system which can be translated into a surface tension value needed on the metal–electrolyte interface to establish a steady state with regard to the energy and mass exchanges.

4. Conclusions

By the way of the local equilibrium approach, the metal–electrolyte interface interaction describes the relationship between surface tension and entropy production on the system. Given that a surface strain work term σdA appears on the entropy production balance, we can conclude that there exists an influence of the surface strain work on the entropy production rate of the system for the metal–electrolyte interface interaction which depends on the surface tension value of the electrolyte.

On behalf of this approach, we have formally introduced time on the estimation of the entropy production, having a way to calculate the charge transfer on time unit for the NED mechanism

by knowing the entropy fluxes on the different phases and doing the ensemble.

The entropy production rate is thought for estimating the degradation on mechanical properties of polycrystalline metals, granted that any system will always be irreversibly evolving to lower states of energy by reducing its mass and therefore, its stress resisting capacity.

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References

- [1] A. Bard, L.R. Faulkner, *Electrochemical Methods*, John Wiley and Sons, New York, 1980.
- [2] J. Ávila, J. Genescá. Más allá de la herrumbre. La ciencia desde México, No. 9. Fondo de Cultura Económica, Mexico, 1986.
- [3] J. Bockris, A. Reedy, M. Gamboa-Aldeco, *Modern Electro-chemistry 2A, Fundamentals of Electronics*, Kluwer Academic/Plenum Publishers, 2000.
- [4] M. Criado, J. Casas, *Termodinámica química y de los procesos irreversibles*, Pearson Addison Wesley, Madrid, 2004.