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NEMCA effect: why are the work function changes of the gas exposed catalyst-electrode surface one-to-one related to the changes in the catalyst working electrode potential?

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Abstract In the present work, an important point concerning the NEMCA effect is addressed. We analyse the reasons why the changes in the work function Φ of the gas exposed catalyst-electrode surface are one to one related to the changes in the catalyst working electrode potential E with respect to a reference electrode. It is concluded that this is due to the unique properties of the catalyst/solid electrolyte interface: the structure of the double layer in this region is very different from that in liquid electrolytes, being the potential difference at this interface mainly determined by the specific adsorption of the mobile species in the solid electrolyte.

Keywords NEMCA · Work function · Catalyst · Electrochemical promotion

Introduction

Although the non-Faradic electrochemical modification of catalytic activity (NEMCA) effect has been widely studied and many of its features are well understood [1, 2, 3], one of its aspects has been the subject of vivid controversy [4, 5, 6, 7]. This refers to the experimental fact that, for many systems, the changes in the work function Φ of the gas exposed catalyst-electrode surface are one-to-one related to the changes in the

ohmic-drop free catalyst working electrode (W) potential E with respect to a reference (R) electrode. This is according to:

$$e\delta E = \delta\Phi \quad (1)$$

where we have used the letter δ to denote changes that can be made arbitrarily small, to make the difference with increments defined below, for which we use the symbol Δ . The main purpose of the present work is not to argue on the validity of Eq. (1), that has been demonstrated experimentally in many cases, but just to point out some of the physical conditions that lead to this equation, all this in terms of a simple physical model for the relevant interfaces that is based on electrostatic considerations.

Discussion

For the sake of clarity, and because the present problem is related in several aspects to the physical concept of electrode potential, in the following discussion we adhere to the notation and model of an electrochemical cell given by Trasatti in his discussions on the concept of the absolute electrode potential [8, 9]. In Fig. 1 we show a half-cell that illustrates the situation of a working electrode in contact with an electrolyte solution. The half-cell corresponding to the reference electrode is omitted for simplicity and the piece of the metal M' is of the same chemical nature as that of the reference electrode. First, we analyse in Fig. 1a the case of an aqueous electrochemical half-cell and then we turn to the problem of an electrode in contact with a solid electrolyte, depicted in Fig. 1b. Trasatti [8, 9] has identified four single-electrode potentials. We use the potentials denoted by him as E_k . These appear as the most general form of electrode potential, since they are obtained when the electrodes are separate and not assembled in a cell. If we consider our working electrode to be made of the metal M , the E_k electrode potential is given alternatively by two equations:

Dedicated to Prof. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry

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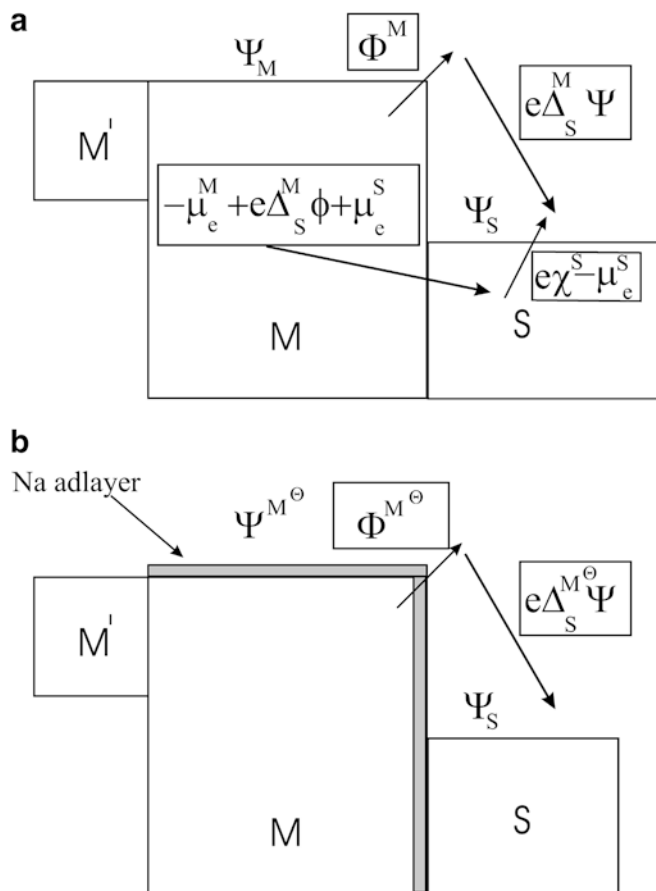


Fig. 1a,b Half-cell illustrating the situation of a working electrode in contact with an electrolyte. The quantities enclosed in *rectangles* denote the different components in which the potential E_k has been decomposed in Eqs. (2), (3) and (9). μ_e^S denotes the chemical potential of the electrons in the solution. The *arrows* indicate the path that an electron would have to follow to have a free energy change corresponding to the corresponding component of the potential: **a** conventional cell with a liquid electrolyte; **b** NEMCA system

$$E_k^M = \Phi^M/e + \Delta_S^M \phi \quad (2)$$

$$E_k^M = -\mu_e^M/e + \Delta_S^M \phi + \chi^S \quad (3)$$

where Φ^M is the work function of the metal M , $\Delta_S^M \phi$, the Volta potential difference between the metal M and the solution, μ_e^M , the chemical potential of the electrons in the metal M , $\Delta_S^M \phi$, the Galvani potential difference between the metal M and the solution, and χ^S is the surface potential of the solution. The components in which the potential has been decomposed in these equations are illustrated in Fig. 1a. The potential E measured with respect to a reference electrode R will be given by

$$E = E_k^M - E_k^R$$

where E_k^R is given by a set of equations similar to Eqs. (2) and (3). In a conventional three-electrode potentiostatic arrangement the potential difference E is controlled by the flow of current between M and a third electrode

(counter electrode). Changes in the measured potential difference can be written according to Eq. (2) as

$$\delta E = \delta(E_k^M - E_k^R) \quad (4)$$

$$= \delta\Phi^M/e + \delta\Delta_R^M \phi - \delta\Phi^R/e \quad (5)$$

$$= \delta\Delta_R^M \phi \quad (6)$$

where we have reasonably assumed that the small electrostatic changes on the surface of the electrodes will leave the work functions unchanged. If we use Eq. (3), the change in the potential difference δE can be decomposed as

$$\delta E = -\delta\mu_e^M/e + \delta\Delta_S^M \phi + \delta\chi^S + \delta\mu_e^R/e - \delta\mu_e^R \phi - \delta\chi^S \quad (7)$$

$$= \delta\Delta_S^M \phi \quad (8)$$

where we have assumed that the reference electrode behaves as an ideally non-polarisable interface. Thus, we have arrived to the well-known result that the measured changes in the potential difference of the cell correspond to the changes in the Galvani's potential difference at the M |solution interface. That is:

$$\delta E = \delta\Delta_S^M \phi = \delta\Delta_S^M \phi$$

Let us now turn to Fig. (1b), representing a half-cell in a solid electrolyte. In the following discussion we shall assume that the solid electrolyte is β'' -alumina¹. This is a solid of formula $\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$, where $n=5-7$ [10]. This solid electrolyte is widely used in the study of the NEMCA effect. The crystalline structure of β'' -alumina consists of close packed layers of oxide anions, stacked in three dimensions, with three quarters of the oxide anions missing in every fifth layer. The Na^+ cations reside in these oxide-deficient layers and have a high mobility, first being reduced at the metal/solid electrolyte interface, diffusing then relatively fast to the metal/gas interface. This phenomenon, called back-spillover [1, 2, 3], allows for the establishment of an equilibrium between Na atoms adsorbed on both interfaces. The equivalent of Eqs. (2) and (3) for this system are

$$E_k^{M^\ominus} = \Phi^{M^\ominus}/e + \Delta_S^{M^\ominus} \phi \quad (9)$$

$$E_k^{M^\ominus} = -\mu^{M^\ominus}/e + \Delta_S^{M^\ominus} \phi + \chi^{se} \quad (10)$$

where M^\ominus denotes the M surface covered by Na atoms at the coverage $^\ominus\text{Na}$ and χ^{se} denotes the surface potential of the solid electrolyte. A remarkable difference with respect to the aqueous system of Fig. 1a is that the work function Φ^{M^\ominus} also changes with the applied potential difference. This is also due to the aforementioned

¹This assumption on the composition of this solid electrolyte is made for concrete discussion purposes. A similar analysis could be made for example with Y203-stabilized ZrO_2 , replacing Na^+ by O^{2-} as conducting ion.

equilibrium of the adsorbed Na atoms between the metal/gas and the metal/electrolyte interfaces. The analogues of Eqs (4) and (7) are now

$$\delta E = \delta(E_k^{M^\ominus} - E_k^R) \quad (11)$$

$$= \delta\Phi^{M^\ominus}/e + \delta\Delta_R^{M^\ominus} \phi - \delta\Phi^R/e \quad (12)$$

$$= \delta\Phi^{M^\ominus}/e + \delta\Delta_R^{M^\ominus} \phi \quad (13)$$

$$\delta E = -\delta\mu_e^M/e + \delta\Delta_{se}^{M^\ominus} \phi + \delta\chi^{se} + \delta\mu_e^R/e - \delta\Delta_{se}^R \phi - \delta\chi^{se} \quad (14)$$

$$= \delta\Delta_{se}^{M^\ominus} \phi \quad (15)$$

Hence we have the equality

$$\delta E = \delta\Phi^{M^\ominus}/e + \delta\Delta_R^{M^\ominus} \phi = \delta\Delta_{se}^{M^\ominus} \phi \quad (16)$$

At this point, we conclude that for Eq. (1) to be valid (that is: $\delta E = \delta\Phi^{M^\ominus}/e$), we must have

$$\delta\Phi^{M^\ominus}/e \approx \delta\Delta_{se}^{M^\ominus} \phi \quad (17)$$

Henceforth $\delta\Delta_R^{M^\ominus} \phi \approx 0$.

The question is now reduced to understand the physical reasons behind the validity of Eq. (17). In order to do this, we must challenge our picture of the (aqueous) double layer when we consider a solid electrolyte.

In Fig. 2 we qualitatively depict the structure of the double layer for an aqueous and a solid electrolyte. The former (Fig. 2a) corresponds to the usual picture of the double layer, well known from textbooks. We have

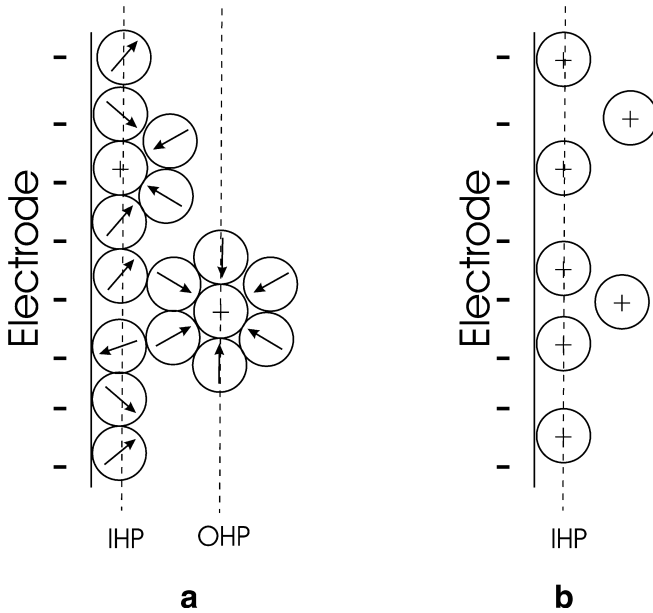


Fig. 2a,b Scheme of cation distribution for: **a** an aqueous (liquid electrolyte) double layer—the inner (IHP) and outer (OHP) Helmholtz planes are noted; **b** a solid electrolyte double layer, for the case where cations are the mobile species—the IHP is noted as well as some cations in the diffuse layer (omitted in a)

contact-adsorbed ions in the inner Helmholtz plane, a compact and a diffuse double layer (not shown). In the case of a solid electrolyte there is no outer Helmholtz plane. This is so because no solvent can prevent the adsorption of the counter-ions. In the case illustrated here, corresponding to β'' -alumina, Na^+ ions accumulate on the surface when the potential is shifted negatively by negative charging the electrode surface. Thus, most of the countercharge corresponds to Na^+ ions in close contact with the metal surface. These contact adsorbed ions are in electronic equilibrium with the metal. We shall see below that only a very small fraction of the Na^+ counter-ions remain at a distance large enough for electronic equilibrium not to be attained. The Na^+ ions in electronic equilibrium with the metal can be envisaged as strongly polarised Na atoms that may migrate to the metal/gas surface.

Let us analyse now why $\delta\Delta_R^{M^\ominus} \phi$ should be small. From the second equality in Eq. (16) we find that $\delta\Delta_R^{M^\ominus} \phi$ should be equal to

$$\delta\Delta_R^{M^\ominus} \phi = \delta\Delta_{se}^{M^\ominus} \phi - \delta\Phi^{M^\ominus}/e \quad (18)$$

We have to consider each of the terms in the rhs of this equation.

From integration of the Poisson equation across the metal/solid-electrolyte interface we can obtain the potential difference $\delta\Delta_{se}^{M^\ominus} \phi$:

$$\delta\Delta_{se}^{M^\ominus} \phi = \phi(\infty) - \phi(-\infty) = 4\pi \int_{-\infty}^{\infty} x \rho_{M^\ominus|se}(x) dx \quad (19)$$

where the ∞ and $-\infty$ denote points well inside the metal M and inside the solid electrolyte respectively, and $\rho_{M^\ominus|se}$ is the charge density distribution at the M /solid-electrolyte interface. All the densities we consider are averaged in the direction parallel to the surface and are functions of the position along the x which is considered to be normal to the interfacial plane. The charge density distribution can be decomposed in

$$\rho_{M^\ominus|se} = \rho_m^+ - n_e + \rho_{Na^+}^{ex} + \rho_{se}^{bulk} \quad (20)$$

where ρ_m^+ is the charge density due to the ion cores in the metal, n_e is the valence electronic density in the metal, $\rho_{Na^+}^{ex}$ is an excess density of Na^+ ions, relative to the density of Na^+ ions in the bulk of the solid electrolyte and ρ_{se}^{bulk} is the charge density of the β'' -alumina skeleton plus a Na^+ concentration corresponding to the bulk of the solid electrolyte. In the following, analysis we assume that the Na^+ ions are the only mobile species in the solid electrolyte, neglecting the electronic polarisation of the solid electrolyte and other relaxation effects on the metal side. In this way, a change in the Galvani potential difference $\Delta_{se}^{M^\ominus} \phi$ (Eq. 19) will be given by

$$\delta\Delta_{se}^{M^\ominus} \phi = 4\pi \int_{-\infty}^{\infty} x (-\delta n_e + \delta \rho_{Na^+}^{ex}) dx \quad (21)$$

Thus, the change in the potential difference across the metal/solid-electrolyte interface induced by the change in the potential difference δE can be envisaged as due to the changes in the electronic density of the metal plus the changes of the distribution of Na^+ ions at the interface.

Let us now consider the second contribution to the rhs of Eq. (18), $\delta\Phi^{M^\ominus}/e$. The work function of a metal contains two contributions: a chemical one and an electrostatic one. In the case of the M^\ominus surface this can be written as

$$\Phi^{M^\ominus} = -\mu_e^M + e\chi^{M^\ominus} \quad (22)$$

where χ^{M^\ominus} is the surface potential of the M^\ominus surface. Since the bulk of M remains unaltered upon polarisation, we have that the change $\delta\Phi^{M^\ominus}/e$ is given by

$$\delta\Phi^{M^\ominus}/e = \delta\chi^{M^\ominus} \quad (23)$$

As in the case of $\Delta_{se}^{M^\ominus}/\phi$ the surface potential χ^{M^\ominus} can be obtained by integration of the Poisson equation across the M^\ominus gas interface:

$$\chi^{M^\ominus} = 4\pi \int_{-\infty}^{\infty} x\rho_{M^\ominus|gas}(x)dx \quad (24)$$

where the ∞ and $-\infty$ denote points well inside the metal M and in the gas respectively, and $\rho_{M^\ominus|gas}(x)$ is the charge density at the M^\ominus /gas interface. As we did in Eq. (20), we decompose this charge density as

$$\rho_{M^\ominus|gas}(x) = \rho_M^+ - n_e + \rho_{Na^+} \quad (25)$$

where n_e is now the electronic density and ρ_{Na^+} is the concentration of Na^+ ions at the $M^\ominus|gas$ interface. From Eqs. (23) and (24) we obtain

$$\delta\Phi^{M^\ominus}/e = 4\pi \int_{-\infty}^{\infty} x(-\delta n_e + \delta\rho_{Na^+})dx \quad (26)$$

and we can now use Eqs. (18), (21) and (26) to obtain

$$\delta\Delta_R^{M^\ominus}/\phi = 4\pi \int_{-\infty}^{\infty} x(\delta n_e - \delta n_e + \delta\rho_{Na^+}^{ex} - \delta\rho_{Na^+})dx \quad (27)$$

Within the present model, this equation shows that the change in the outer potential difference $\Delta_{ref}^{M^\ominus}/\phi$ reflects the difference metal/gas in the changes of the profiles of electronic and ionic densities at the metal/gas and metal/solid-electrolyte interfaces. Thus, the only way to understand why Eq. (1) is valid is to claim that the electronic and ionic changes at the metal/gas and the metal/electrolyte interfaces upon polarisation are essentially the same. This is not hard to understand for the changes in the electronic profile if the change of the change of the total ionic charge is the same. According to jellium density-functional calculations [12], when a low electronic density adsorbate is deposited on a large

electronic density substrate, the changes in the electronic density are similar to those induced by an external charge located relatively far from the surface. In other words, the changes in the electronic density should be largely independent on the way in which the positive countercharge is distributed. More difficult to understand is the fact that Na^+ ions at the metal/solid electrolyte interphase should have the same changes in their distribution as in the metal/gas interphase. In the former case, part of the Na^+ ions are contact-adsorbed, but part of them may be in the diffuse layer as well. In the latter case, except for very few Na atoms in the gas phase, practically all the Na^+ ions will be adsorbed on the surface. To elucidate the former question, we must consider that the contact-adsorbed Na^+ ions are essentially in the same physical situation as those in the metal/gas interface, and they can freely migrate between both interfaces (by the back-spillover mechanism). Thus, the main difference between $\delta\rho_{Na^+}^{ex}$ and $\delta\rho_{Na^+}$ will be given by those Na^+ cations participating in the diffuse layer. We can get a rough estimation of the extent of this diffuse layer by calculating the Debye length L_D for the solid electrolyte, which is given by

$$L_D = \sqrt{\frac{\epsilon\epsilon_0 kT}{2z^2 e^2 n^0}} \quad (28)$$

If we use for n^0 the concentration of Na^+ ions in β'' -alumina we obtain

$$L_D = \sqrt{\epsilon} 0.13 \text{ \AA} \quad (29)$$

so that reasonable values of ϵ yield L_D s of the order of one \AA or less. This justifies the scheme of the metal/solid electrolyte interface given in Fig. 2b, where practically all the Na^+ ions are contact adsorbed. According to this, the changes of potential difference at the solid-electrolyte interface are achieved by changing the coverage degree of strongly polarized Na atoms. The reason why the changes $\delta\rho_{Na^+}^{ex}$ and $\delta\rho_{Na^+}$ are essentially equal in the close neighbourhood of the metal surface can be sought in the fact that the densities of Na^+ ions in this region should be very similar. Thinking of Na^+ ions as positive charges under the influence of an electrostatic potential, it can be inferred that their concentrations in the neighbourhood of the surface of the catalyst should be the same at the metal/gas and at the metal/solid electrolyte interfaces because the chemical potentials of the Na^+ ions must be the same at both interfaces, since they are free to migrate between them. The electrostatic potential at both surfaces of the catalyst must be the same, since they are in electronic equilibrium and the catalyst is the same (same chemical potential of the electrons).

It must also be mentioned that the present problem shares some common features with the problem of the emersed double layer[13, 14, 15, 16] and the problem can be analysed from the same point of view. The term emersion is used in these works to describe the

withdrawal of an electrode from solution into either an inert atmosphere or into vacuum. The results obtained by Hansen and Kolb in concentrated electrolytes [13] show that the work function of the electrodes is independent of their material, presenting a linear dependence with unity slope upon the electrode potential applied before and during emersion. This was found to be an evidence for nearly complete retention of the double layer after removal. Subsequent work by Katz et al. [15] under UHV conditions led to the conclusion that counterions are the main species adsorbed on the emersed surfaces, remaining small quantities of water that preserve the distance between the ions and the surface of the electrode. This must be so because loss of these molecules would lead to a rearrangement of the counterions, with a concomitant change in the work function. In short, the space distribution of free charge is kept upon double layer emersion.

We can now make the following association. In the case of the emersed double layer experiments we have the following change:

- Immersed double layer → emersed double layer while in the case of the NEMCA system we can write
- Catalyst/solid electrolyte double layer → catalyst/gas interphase.

We propose that in the second case the *space distribution of free charge* must be essentially the same for the relationship $e\delta E = \delta\Phi$ to be valid. Tsiplakides and Vayenas [17] have pointed out that when Na^+ is supplied to the gas/catalyst interphase, Na adatoms form a (12×12) overlayer on top of a (2×2) adlattice over the entire Pt/gas interface. Thus, we suggest that the catalyst/solid electrolyte interphase should exhibit a similar structure. This should be true at least in the neighbourhood of the three phase boundary, or more generally in the region where the potential changes δE are operative to electroadsorb the Na^+ ions.

Since the discussion given above supports the view of Vayenas and coworkers in recent work [17, 18, 19, 20] and shares several common points with it, it is worth to point out what new insight is brought in. First, our discussion emphasises on the role of the *charge distribution* at the interphases involved in determining the observed changes in potential difference or work function. This can be analysed only through the integration of the Poisson equation across the interphases involved, as we did. For example, Eq. (27) shows that changes in the electronic density and ionic profiles should be closely compensated for Eq. (1) to be valid. Second, if such a compensation occurs, the catalyst/gas and the catalyst/solid electrolyte interphases should be described on the same footing. This is not mentioned in the current modelling of the NEMCA effect.

Conclusions

When the potential difference applied to the catalyst/solid electrolyte interface is varied in a NEMCA system, a change occurs in the extent of the specific adsorption of the ions participating in the conductivity of the solid electrolyte. This change in the surface concentration of ionic species (i.e. Na^+ , O^{2-}) makes the largest contribution to the changes in the potential difference across the interface. Due to the high concentration of ions the contribution of the diffuse double layer is minor. The specifically-adsorbed ions are able to reach the metal-catalyst/gas interface (“back-spillover”), so that a surface concentration profile appears there which practically mimics that of the metal-catalyst/solid-electrolyte interface. The changes of the work function $\delta\Phi$ at the metal/gas interface and the changes of the potential difference $e\delta E$ at the metal/solid-electrolyte interface are given by the same equation, which contains the changes of the concentrations of ionic species. Since these are practically equal, identical values of $e\delta E$ and $\delta\Phi$ result.

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