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The non-integer cyclovoltammetric electron-exchange numbers of reversible redox reactions of adsorbates

2. Coupled protonation: theoretical considerations

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Abstract Allowing for the interfacial potential distribution it can be shown that the apparent faradaic electron number, n'_{app} , of ad-layers of chemically modified electrodes and the surface redox valency, n' , relating to the slope of the peak potential/pH response [Huck (2002) J Solid State Electrochem 6:534] are at least identical, having the same thermodynamic origin. n'_{app} is calculated from the cyclovoltammetric (CV) peak areas above the interpolated base line. At $v_{\text{H}^+} = n$ for proton-coupled surface redox reactions, the influence of the potential drop of the diffuse double layer disappears because the capacitor of the corresponding equivalent circuit becomes shortened by proton transfer, whereby the otherwise non-integer n'_{app} or n' values now approach the integer electron numbers, n , of the Nernst equation.

Keywords Chemically modified electrodes · Cyclic voltammetry · Double layer · Adsorption

Introduction

It has been reported previously that the CV peak area above the interpolated base line of a redox active adsorbate corresponds to an apparent charge Q_{app} , which is smaller than the theoretical faradaic charge Q [1]. The calculation originated from the capacitive equivalent circuit consisting of two capacitors arranged in parallel with redox pseudocapacitance, C_{ps} , and the inherent capacitance, C_1 , of the redox-inactive backbone. C_1 and C_{ps} should be in series with the diffuse-layer capacitance, C_d . That simplified equivalent circuit corresponds to the interfacial potential distribution (IPD) model of self-assembled monolayers reported by Smith and White [2], whereby discreteness-of-charge

effects [3, 4] and possible ion-pairing equilibria with counterions [5, 6] were not taken into consideration.

In this study the former calculations referring to reversible redox reactions without protonation, i.e.



are extended to proton-coupled electron transfers according to



It will be shown that in the special case of $v = n$ the CVs are no longer influenced by the diffuse double layer. Earlier experiments [1, 7] with flavin adenine dinucleotide (FAD) adsorbed onto graphite electrodes were reinterpreted.

Theoretical considerations

The influence of interfacial potential distribution

The Nernst equation of redox reaction (2) can be written as

$$E = E'_0 + \phi_1 + \frac{RT}{nF} \ln(\Gamma_{\text{O}} c_{\text{H}^+}^v / \Gamma_{\text{R}}) \quad (3)$$

including

$$c_{\text{H}^+} = c_{0,\text{H}^+} \exp(-F\phi_1/RT) \quad (4)$$

where E'_0 is a formal potential of the surface redox reaction dependent on the adsorption coefficients and lateral interaction parameters [1] of the redox couple and $c_{0,\text{H}}$ the bulk concentration of H^+ . ϕ_1 refers to the potential drop of the diffuse double layer [2]. The other symbols have their usual significance. Equation (4) accounts for the concentration of the protons at the ad-layer as a function of ϕ_1 . The following derivation originates from the non-measurable Galvani potentials ϕ_{M} of the electrode and $\phi_1 = \phi_{\text{PET}} = \phi_{\text{PPT}}$ at the plane of electron or proton transfer, respectively, with respect to

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the solution potentials $\phi_S=0$. Setting $U=U_1+U_2=\phi_M-\phi_S$ for the entire potential drop at the interface with $U_1=\phi_M-\phi_1$ and $U_2=\phi_1-\phi_S=\phi_1$, Eq. (3) becomes in the absence of lateral interaction at $\Gamma_T=\Gamma_O+\Gamma_R \rightarrow 0$

$$U = U_0 + (1 - \nu/n)\phi_1 + \frac{RT}{nF} \ln(\Gamma_O c_{0,H^+}^\nu / \Gamma_R) \quad (5)$$

where U_0 is the inner potential drop at $\Gamma_O=\Gamma_R$. Furthermore, U_1 and $U_2=\phi_1$ can be expressed as functions of C_1 and C_d : outside of the CV wave at $C_{ps}=0$ the total capacitance C_T of the double layer is given by

$$1/C_T = 1/C_1 + 1/C_d \quad (6)$$

whereas the relative potential drops are

$$U_1/U = C_T/C_1 = 1/(1/C_1 + 1/C_d)C_1 = 1/(1 + C_1/C_d) \quad (7)$$

and

$$U_2/U = \phi_1/U = C_T/C_d = 1/(1/C_1 + 1/C_d)C_d = 1/(1 + C_d/C_1) \quad (8)$$

As presented in [1] Eq. (7) also applies to the relative apparent charge Q_{app}/Q over the interpolated base line. It follows that Eqs. (7) and (8) also account for the effective relative potential drops U_1/U and $U_2/U=\phi_1/U$ within the CV peak at $C_{ps} \neq 0$ [1]. However, according to the Gouy–Chapman theory [8], C_d varies with potential and bulk electrolyte concentration. For that reason C_1/C_d refers to a mean value of the two C_1/C_d values before and after the CV peak, which can be calculated from the corresponding measurable total capacities C_T at the base line. From Eq. (6) it follows that

$$C_1/C_d = C_1/C_T - 1 \quad (9)$$

where C_1 is determined by

$$C_1 = \epsilon_0 \epsilon_1 / d_1 \quad (10)$$

with ϵ_0 the permittivity, ϵ_1 the dielectric constant and d_1 the thickness of the ad-layer. In considering these IPD relation Eq. (5) can be further evaluated. Substituting Eq. (8) into Eq. (5) yields

$$U = U_0 + (1 - \nu/n) \frac{U}{1 + C_d/C_1} + \frac{RT}{nF} \ln(\Gamma_O c_{0,H^+}^\nu / \Gamma_R) \quad (11)$$

Solving Eq. (11) for U gives

$$U = \frac{1}{1 - \frac{1-\nu/n}{1+C_d/C_1}} \left[U_0 + \frac{RT}{nF} \ln(\Gamma_O c_{0,H^+}^\nu / \Gamma_R) \right] \quad (12)$$

$$= U'_0 + \frac{RT}{n_{app}F} \ln(\Gamma_O c_{0,H^+}^\nu / \Gamma_R) \quad (13)$$

defining

$$n_{app} = n \left(1 - \frac{1 - \nu/n}{1 + C_d/C_1} \right) = \frac{n + \nu C_1/C_d}{1 + C_1/C_d} \quad (14)$$

and

$$U'_0 = \frac{n}{n_{app}} U_0 \quad (15)$$

Equation (14) involves two special cases of interest. At $\nu=0$ it simplifies to

$$n_{app} = \frac{n}{1 + C_1/C_d} \quad (16)$$

as presented by Eq. (19) in [1] and at $\nu=n$ or $C_d \gg C_1$ at high supporting electrolyte concentration to

$$n_{app} = n \quad (17)$$

At $\nu=n$ the proton-coupled surface redox reaction becomes independent of the potential drop of the diffuse double layer because the C_d appears to be shortened by proton transfer. The use of Eq. (13) also allows calculation of all other quantities related to the Nernst equation. However, for practical purposes the non-measurable potential drops U and U'_0 must first be replaced by the measurable potentials E and E_0 with respect to $\phi_{M(ref)}$ of a reference electrode.

To do so Eq. (13) combined with Eq. (15) can be rewritten as

$$\begin{aligned} \phi_M - \phi_{M(ref)} &= E = \frac{n}{n_{app}} \phi_M^0 - \phi_{M(ref)} + \frac{RT}{n_{app}F} \ln(\Gamma_O c_{0,H^+}^\nu / \Gamma_R) \\ &= \frac{n}{n_{app}} [\phi_M^0 - \phi_{M(ref)}] + \left(\frac{n}{n_{app}} - 1 \right) \phi_{M(ref)} + \dots \\ &= \frac{n}{n_{app}} E'_0 + \left(\frac{n}{n_{app}} - 1 \right) \phi_{M(ref)} + \dots \\ &= E'_0 + \frac{RT}{n_{app}F} \ln(\Gamma_O c_{0,H^+}^\nu / \Gamma_R) \end{aligned} \quad (18)$$

where $\phi_{M(ref)}$ or $\phi_{M(ref)}-\phi_S$ is related to the potential of zero charge (PZC) of the uncoated substrate electrode with respect to the reference electrode [2, 5].

Thus, the consecutive equations of Eq. (13) can be written as

$$N_{ox} = \frac{N_T}{1 + \exp[-n_{app}F(E - E'_0)/RT]} \quad (19)$$

$$Q_{app} = \frac{n_{app}FN_T}{1 + \exp[-n_{app}F(E - E'_0)/RT]} \quad (20)$$

and

$$\begin{aligned} i_{app} &= \frac{dQ_{app}}{dt} \\ &= \frac{n_{app}^2 F^2 N_T \nu \exp[-n_{app}F(E - E'_0)/RT]}{RT \{ 1 + \exp[-n_{app}F(E - E'_0)/RT] \}^2} = C_{ps,app} \nu \end{aligned} \quad (21)$$

where N_T is the total number of adsorbed molecules, ν the scan rate of the outer voltage and C_{ps} the redox pseudocapacitance. If the potential ranges from $E - E'_0 = -\infty$ to ∞ Eq. (20) yields the apparent total charge of the CV peak over the interpolated base line

$$Q_{\text{app}} = n_{\text{app}} F N_{\text{T}} \quad (22)$$

In the absence of lateral interaction [9, 10, 11, 12] at $\Gamma_{\text{T}} \rightarrow 0$ and disproportionation equilibria of two separate electron transfers [13] the total width $b_{1/2}$ at half-height of the CV wave becomes

$$b_{1/2} = \frac{90.6}{n_{\text{app}}} \text{mV} \quad (25^\circ \text{C}) \quad (23)$$

In the case of lateral interaction, n of the corresponding equations must also be replaced by n_{app} . The peak current i_{p} for instance can be expressed as

$$i_{\text{p}} = \frac{n_{\text{app}}^2 F^2 N_{\text{T}} v}{RT[4 - \Gamma_{\text{T}}(r_0 + r_{\text{R}})]} \quad (24)$$

where $r_0 = r_{00} - r_{0\text{R}}$ and $r_{\text{R}} = r_{\text{RR}} - r_{\text{R}0}$ are the parameters for 00, RR, 0R and R0 lateral interactions.

Contributions of additional potential-dependent parameters

Introducing the differential quotients $d\Delta G_{\text{ad}}/dE$ of the oxidized and reduced species and also $d\phi_1/dE$ in a similar manner the surface redox valency n' for the pH dependence of the peak potential E_{p} was calculated [1]. From Eq. (8) it follows for $d\phi_1/dE$

$$d\phi_1/dE = 1/(1 + C_{\text{d}}/C_1) \quad (25)$$

Substituting Eq. (25) into Eq. (33) in [1] yields

$$\begin{aligned} \Delta E_{\text{p}}/\Delta \text{pH} &= \frac{2.303vRT/nF}{1 - \frac{1-v/n}{1+C_{\text{d}}/C_1} + \frac{d}{dE}(\Delta G_{\text{R,ad}} - \Delta G_{0,\text{ad}})/nF} \\ &= \frac{2.303vRT/nF}{n_{\text{app}} + \frac{d}{dE}(\Delta G_{\text{R,ad}} - \Delta G_{0,\text{ad}})/F} = 2.303vRT/n'F \end{aligned} \quad (26)$$

where

$$n' = n_{\text{app}} + \frac{d}{dE}(\Delta G_{\text{R,ad}} - \Delta G_{0,\text{ad}})/F = n'_{\text{app}} \quad (26\text{a})$$

Taking into account the differential quotients of the free adsorption energies n_{app} in Eq. (26a) has to be replaced by the more complex electron number n'_{app} , whereby n' relates to the slope of the E_{p}/pH dependence and n'_{app} to the faradaic charge of the CV peaks. At equal differential free adsorption energies n'_{app} would agree with n_{app} of Eq. (14) or Eq. (16), respectively. An exact derivation for $n' = n'_{\text{app}}$ is given in the Appendix starting from the Nernst equation as their common thermodynamic basis. Consequently n_{app} in Eqs. (18, 19, 20, 21, 22, 23, 24) can be replaced by n'_{app} or by the more easily measurable n' . As described above other differential quotients of possible potential-dependent quantities, such as lateral interaction coefficients, could also be introduced in certain cases.

The true base line

The true base-line current i_{00} should be defined as a theoretical background current being related to true peak currents, which yield the true faradaic charge after integration over the whole peak. Q_{true} should refer to thin-layer voltammetry with dissolved species. Initially i_{true} was expressed by an unmodified equation using the integer electron number, n [1]. Now the non-integer n'_{app} of Eq. (26a) should be applied. Then i_{app} is given by Eq. (21) and i_{true} by

$$n i_{\text{true}} = \frac{n}{n'_{\text{app}}} i_{\text{app}} = \frac{n}{n'_{\text{app}}} C_{\text{ps,app}} v \quad (27)$$

The further calculation follows the steps as previously described and which are illustrated in Fig. 2 of [1]. i'_{app} should be the supplementary current between the interpolated and the true base-line currents i_0 and i_{00} . Then it holds that

$$i'_{\text{app}} = \left(\frac{n}{n'_{\text{app}}} C_{\text{ps,app}} - C_{\text{ps,app}} \right) v = \left(\frac{n}{n'_{\text{app}}} - 1 \right) C_{\text{ps,app}} v \quad (28)$$

and i_{00} becomes

$$i_{00} = i_0 - i'_{\text{app}} = \left[\frac{1}{1/C_1 + 1/C_{\text{d}}} - \left(\frac{n}{n'_{\text{app}}} - 1 \right) C_{\text{ps,app}} \right] v \quad (29)$$

reaching a minimum for $n'_{\text{app}} < n$ at the peak potential [1, 2] (or a maximum for $n'_{\text{app}} > n$), where $C_{\text{ps,app}}$ has a maximum.

Discussion: reinterpretation of earlier experiments

At present no systematic experimental work exists, which compares n_{app} or n'_{app} of background-subtracted peak areas with n' of E_{p}/pH relations. As an example of a $2\text{H}^+/2\text{e}^-$ transfer the adsorption of FAD onto a graphite electrode was presented [1]. The mean slope $\Delta E_{\text{p}}/\Delta \text{pH}$ was 60 mV/pH at $v = 100 \text{ mV s}^{-1}$ [14] indicating $v/n' = 1$. n'_{app} could not be directly estimated with sufficient accuracy. Therefore the relative peak areas A/A_0 in 0.1 M phosphate buffer of pH 7 without (A) and with 1 M NaCl (A_0) as supporting electrolyte at different scan rates v were measured and extrapolated to $v = 0$, thus eliminating overvoltages¹. The limiting value A/A_0 was 0.897 (Table 1 of [1]) based upon a calculation of the peak areas using the relative products of peak height,

¹At $v > 0$ ohmic resistances had to be introduced in the given simplified equivalent circuit. Then algebraic expressions for n' or n'_{app} could no longer be evaluated. In contradiction to the small slope of Fig. 1a under reversible conditions the A/A_0 values should be independent of v . Furthermore, at too high sweep rates Eq. (4) relating to equilibrium concentrations of H^+ at the surface would become invalid.

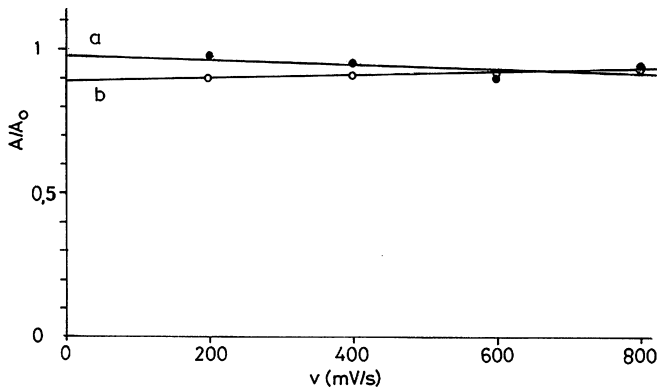


Fig. 1a, b Dependence of the relative peak areas A/A_0 for 2 nanomoles FAD as adsorbate on a spectrographic graphite rod of 6 mm diameter (Ringsdorff-Werke) in 0.1 M phosphate buffer of pH 7 with (A_0) and without 1 M NaCl (A) as supporting electrolyte at different scan rates mV s^{-1} . **a** Gravimetric values of cutout peaks. **b** Relative products of peak height, h , and peak width at half-height, $b_{1/2}$

h , and peak width at half height, $b_{1/2}$, (straight line b of Fig. 1). The earlier illustrative calculation of n'_{app} values would only be valid for $v \neq n$. However, using the gravimetrically evaluated cutout peaks of the anodic scans A/A_0 is 0.980 ± 0.034 at $v=0$ according to the straight line a of Fig. 1, where in agreement with Eqs. (14) and (22) at $v=n$ the measurements are independent of C_d of the diffuse double layer. At $d(\Delta G_{\text{R,ad}})/dE = d(\Delta G_{0,\text{ad}})/dE$ for the relative large FAD molecule Eq. (26) would yield $n_{\text{app}} = n'_{\text{app}} = n' = n$. This difference between the two extrapolated A/A_0 values can be formally attributed to the occurrence of peak tailings, which lead to inaccurate A/A_0 values for $hb_{1/2}$ measurements.

Conclusions

Whereas in the previous contribution non-integer apparent faradaic and Nernstian electron numbers n_{app} and n' were introduced, it has now been shown that n'_{app} and n' should be identical. In the special case of $v=n$ of proton-coupled electron transfer, the equations become independent of the potential drop or the capacitance at the diffuse double layer. If the electroactive ad-layer is covered with an additional electroinactive layer with the capacitance C_2 , $1/C_d$ must be replaced by $1/C_d + 1/C_2$ leading to a drastic peak shortening and broadening [2]. However, the calculations are then complicated by the occurrence of ohmic resistances. Further experimental work must be done to confirm the deduced equations.

Finally, it should be noted that no expressions for electrosorption processes have been presented. These were characterized by a fractional electrosorption valency, γ , which refers to partial charge transfer of chemisorbed species [15, 16, 17, 18, 19, 20]. However, partial charge transfers should be already involved in the differential free adsorption energies in Eq. (26).

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Appendix

Introducing the Galvani potentials and the free adsorption energies of the reactants the Nernst equation referring to the redox reaction of Eq. (5) can be written as

$$U = U_0 + (1 - v/n)\phi_1 + (\Delta G_{0,\text{ad}} - \Delta G_{\text{R,ad}})/nF + \frac{RT}{nF} \ln(\Gamma_{\text{O}} c_{\text{H}^+}^v / \Gamma_{\text{R}}) \quad (30)$$

Differentiation of Eq. (30) with respect to the peak potential E_p leads to Eq. (26) describing the slope of the E_p/pH response and to Eq. (26a) or Eq. (33) in [1] defining the electron number n' . In order to get the apparent faradaic charge Q'_{app} by integration over the CV peak [1] or n'_{app} , respectively, Eq. (30) may be rewritten as

$$U - \phi_1 = U_1 = U_0 - \frac{v}{n}\phi_1 + (\Delta G_{0,\text{ad}} - \Delta G_{\text{R,ad}})/nF + \frac{RT}{nF} \ln(\Gamma_{\text{O}} c_{\text{H}^+}^v / \Gamma_{\text{R}}) \quad (31)$$

whereby the effective potential drop U_1 is used. Introducing the potential-dependent parameters ϕ_1 and ΔG_{ad} Eq. (31) becomes

$$U_1 = U'_0 - \frac{d}{dU_1} \left[\frac{v}{n}\phi_1 + (\Delta G_{\text{R,ad}} - \Delta G_{0,\text{ad}})/nF \right] U_1 + \frac{RT}{nF} \ln(\Gamma_{\text{O}} c_{\text{H}^+}^v / \Gamma_{\text{R}}) \quad (32)$$

and by solving for U_1

$$\left\{ 1 + \frac{d}{dU_1} \left[\frac{v}{n}\phi_1 + (\Delta G_{\text{R,ad}} - \Delta G_{0,\text{ad}})/nF \right] \right\} U_1 = U'_0 + \frac{RT}{nF} \ln(\Gamma_{\text{O}} c_{\text{H}^+}^v / \Gamma_{\text{R}}) \quad (33)$$

and

$$U_1 = U_{01} + \frac{RT}{n_x F} \ln(\Gamma_{\text{O}} c_{\text{H}^+}^v / \Gamma_{\text{R}}) \quad (34)$$

defining the formal electron number n_x

$$n_x = \left\{ 1 + \frac{d}{dU_1} \left[\frac{v}{n}\phi_1 + (\Delta G_{\text{R,ad}} - \Delta G_{0,\text{ad}})/nF \right] \right\} n \quad (35)$$

and

$$U_{01} = \frac{n}{n_x} U'_0 \quad (36)$$

According to Eq. (18) in [1] Q'_{app} is given by the integral

$$Q'_{\text{app}} = \frac{1}{1 + C_1/C_d} \int_{-\infty}^{\infty} c_{\text{ps}} d(U_1 - U_{01}) = \frac{n_x F N_{\text{T}}}{1 + C_1/C_d} = n'_{\text{app}} F N_{\text{T}} \quad (37)$$

where now n of the unmodified Nernst equation is replaced by n_x and U_0 by U_{01} taking into account that C_{ps} is derived from the Nernst equation by differentiation, whereas the integration follows the opposite way.

Comparing the two derivations for n' and n'_{app} it can be seen that different differential quotients are used: for n' the differentiation is carried out with respect to the whole potential drop U but for n'_{app} only to the smaller effective potential drop U_1 . The identity of n'_{app} with n' follows from the conversion of Eq. (38). It holds that

$$\begin{aligned} \frac{1}{1 + C_1/C_d} \frac{dx}{dU_1} &= \frac{1}{1 + C_1/C_d} \frac{dx}{dU} \frac{dU}{dU_1} \\ &= \frac{1}{1 + C_1/C_d} (1 + C_1/C_d) \frac{dx}{dU} = \frac{dx}{dU} \end{aligned} \quad (38)$$

where dU/dU_1 is given by Eq. (7). Finally, the combination of Eqs. (35, 36, 37, 38) yields $n'_{app} = n'$ as follows

$$\begin{aligned} n'_{app} &= \frac{n_x}{1 + C_1/C_d} \\ &= \frac{1}{1 + C_1/C_d} \left\{ 1 + \frac{d}{dU_1} \left[\frac{v}{n} \phi_1 + (\Delta G_{R,ad} - \Delta G_{0,ad})/nF \right] \right\} n \\ &= \left[\frac{1}{1 + C_1/C_d} + \frac{v}{n} \frac{1}{1 + C_1/C_d} + \frac{d}{dU} (\Delta G_{R,ad} - \Delta G_{0,ad})/nF \right] n \\ &= \frac{n + vC_1/C_d}{1 + C_1/C_d} + \frac{d}{dU} (\Delta G_{R,ad} - \Delta G_{0,ad})/F = n' \end{aligned} \quad (39)$$

where the quotient of the last row agrees with n_{app} of Eq. (14).

Supplement

The beginning of the second row of the product of Eq. (32) in [1] should be written with a multiplication sign.

References

1. Huck H (2002) *J Solid State Electrochem* 6:534
2. Smith CP, White HS (1992) *Anal Chem* 64:2398
3. Fawcett WR (1994) *J Electroanal Chem* 378:117
4. Creager SE, Rowe GK (1997) *J Electroanal Chem* 420:291
5. Ohtani M, Kuwabata S, Yoneyama H (1997) *Anal Chem* 69:1045
6. Andreu R, Calvente JJ, Fawcett WR, Molero M (1997) *J Phys Chem B* 101:2884
7. Huck H (1980) *Z Phys Chem NF* 120:39
8. Bard AJ, Faulkner LR (2001) *Electrochemical methods*. Wiley, New York, Chap 11, p 13
9. Smith DF, Willman K, Kuo K, Murray RW (1979) *J Electroanal Chem* 95:217
10. Brown AP, Anson FC (1977) *Anal Chem* 49:1589
11. Laviron E (1974) *J Electroanal Chem* 52:395
12. Laviron E (1982) In: Bard AJ (ed) *Electroanalytical chemistry*, vol 12. Marcel Dekker, New York, Chap. 2
13. Huck H (1981) *Ber Bunsenges Phys Chem* 85:221
14. Gorton L, Johansson G (1980) *J Electroanal Chem* 113:151
15. Vetter KJ, Plieth WJ (1968) *Z Phys Chem NF* 61:282; (1969) 65:189
16. Vetter KJ, Plieth WJ (1968) *Phys Chem* 72:673; (1969) 73:79
17. Schultze JW (1970) *Ber Bunsenges Phys Chem* 74:705
18. Vetter KJ, Schultze JW (1972) *Ber Bunsenges Phys Chem* 76:920; 76:927
19. Schultze JW, Vetter KJ (1973) *J Electroanal Chem* 44:63
20. Rolle D, Schultze JW (1987) *J Electroanal Chem* 229:141