Naphthoquinone–silicate based gas electrodes: chemical–electrochemical mode of operation

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Abstract

We demonstrate a new type of gas electrode composed of a porous matrix of carbon powder and redox polymer binder. Homogenous reaction of the target gaseous compound with the redox functional groups of the polymer produces a concentration gradient within the redox polymer. This gradient induces charge transport towards the carbon particles where electrode regeneration of the redox groups takes place.

Oxygen reduction on a naphthoquinone-modified carbon ceramic composite electrode (NPQ/CCE) demonstrates a new type of gas permeable electrode. A reaction–diffusion model for the gas electrodes is presented. The model predicts electrochemical charge transfer control at low overpotentials and either kinetic control or diffusion limitation at high overpotentials. Predicted current–potential curves of the composite electrode are compared to the observed polarization curves for oxygen reduction on redox–silicate–carbon gas electrodes. Oxygen sensing on NPQ-modified CCE is demonstrated. © 2001 Published by Elsevier Science B.V.

Keywords: Sol–gel; Redox polymers; Silicate; Carbon ceramic electrodes; Gas electrodes

1. Introduction

Gas permeable electrodes are porous hydrophobic electrodes through which gaseous reactants penetrate through the backside of the electrode and reach the solid | liquid interface or catalytic sites on this interface where charge transfer takes place (see Scheme 1). Mass transport across the liquid film becomes the limiting step at high overpotentials. Thus, minimization of the thickness of the liquid film adjacent to the carbon powder becomes a major technological challenge. Catalysis is most efficiently accomplished by perfluoroplastic, hydrophobic polymer binders such as Teflon, PVDF or PTFE [1,2]. Additional inert metal or pyrolyzed organometallic catalysts are used to enhance charge transport at the solid | liquid interface.

In this article we examine oxygen reduction on a novel class of gas electrodes which is illustrated in Scheme 2. These electrodes rely on the electrochemical conductivity of redox polymer binders and do not require precious metal catalysts. Oxygen diffuses through the backside of the electrode, and reaches the

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Scheme 2. Oxygen reduction on redox polymer-modified carbon ceramic gas electrodes.

We exemplify this type of gas electrode by a composite material made of carbon powder and a naphthoquinone-functionalized silicate binder. Oxygen reduction to hydrogen peroxide serves as a demonstrative test case. The redox binder was produced by sol–gel polymerization of 2-chloro-3-[2-(dimethyl(3-trimethoxysilyl)propylammonio)ethyl]amino]-1,4-naphthoquinone bromide (NPQ in Scheme 3). NPQ was first synthesized by Wrighton and coworkers [3] and used to catalyze the conversion of oxygen to hydrogen peroxide on coated metal electrodes. Here we show that it can be used in conjunction with carbon powder for the production of gas permeable electrodes. In order to endow hydrophobicity and prevent complete flooding of the redox-modified carbon ceramic electrode we added methyltrimethoxysilane, MTMOS, to the sol–gel precursors. The effect of the combination of NPQ and the hydrophobic monomer was examined.

Selection of a silicate-based binder in these studies was motivated more by a desire to demonstrate yet another unconventional application of sol–gel-derived carbon ceramic composite electrodes (CCE) than by the relative efficiency of carbon ceramic electrodes for high-duty applications. Several reviews of sol–gel electrochemistry have recently appeared [4–8]. Additionally, it is rather easy to fabricate flooded section CCEs by the sol–gel technology. This configuration is most useful for sensing applications where high signals are less important compared to the minimization of evaporation losses [9–12]. The smaller liquid | gas interface area in the flooded electrode configuration limits the evaporation losses. We anticipate that redox-modified carbon wetted section at the bottom of the electrode where it reduces oxidized moieties on the redox polymer; then charge transport towards the carbon network is carried out by a self-exchange mechanism. An electrodic pro-
fluoroplastic polymer electrodes will function in a simi-
lar way and perhaps even exhibit larger signals due to
their wetted channel configuration [1]. Selection of the
naphthoquinone catalyst was motivated by the advan-
tageous properties of this catalyst. Its formal potential
at neutral pH ($E^* = -0.350$ mV versus Ag | AgCl at
pH 7.0) is much higher than that required for oxygen
reduction on carbon electrodes and it reacts rapidly
with oxygen to give hydrogen peroxide without addi-
tional catalysts. Hydrogen peroxide is a potentially
useful product and, in fact, the most popular commer-
cial process for hydrogen peroxide generation is via the
reduction of oxygen by anthrahydroquinone and subse-
quent reductive regeneration of the anthraquinone by
hydrogen gas [13]. An additional incentive for the use
of quinone catalysts in this process comes from their
fast electrochemical kinetics [14]. The mathematical
manifestation of these three intuitive requirements will
be discussed in Section 3.

2. Experimental

2.1. Chemicals

2,3-Dichloro-1,4-naphthoquinone, $N,N$-dimethyl-
dimethylenediamine and tetramethoxysilane (TMOS)
were purchased from Aldrich. 3-Bromopropyl-
trimethoxysilane was purchased from ABCR (Karl-
sruhe, Germany). All other chemicals were analytical
grade. Solutions were prepared with triply distilled
water.

Synthesis of 2-chloro-3-$[2$-(dimethyl$)3$-(trimethoxy-
ilyl)$propyl]amino$ethyl$ amino$]-1,4-naphthoquinone
bromide, I was performed following Wrighton’s proto-
col (Scheme 3) [3]. First, 2-chloro-3-$[2$-(dimethyl-
amino)$ethyl]amino$]-1,4-naphthoquinone, III was syn-
thesized by refluxing ethanol solution containing $N,N$-
dimethylenediamine and 2,3-dichloro-1,4-naphtho-
quinone. After cooling, the red chloride salt of III
was precipitated, filtered, extracted into CH$_2$Cl$_2$ and
then dried and filtered again. The solvent was removed
under vacuum to obtain III. Mixing 1 g of III in 3 ml
of 3-bromopropyltrimethoxysilane at 90°C for 12 h
precipitated IV. IV was then filtered, washed with hex-
ane and purified by vacuum evaporation. H NMR
studies confirmed the identity and purity of IV.

2.2. Electrode preparation

Preparation of NPQ sol: The NPQ monomer (20 mg)
was partially dissolved in 1.5 ml methanol. Water (2
ml) was then added dropwise under vigorous stirring.
After 10 min 0.1 M phosphate buffer solution (pH 7.0)
was added to give a final concentration of ca. 2 mM of
IV in the sol. The sol was kept at room temperature
(r.t.) for months with no change in its visible character-
istics. The sol was not deposited on the glass beaker.

2.2.1. Preparation of glassy carbon coated electrodes

Preparation of glassy carbon coated electrodes

Preparation of glassy carbon coated electrodes: The GC
disk electrode was first polished with 600 grit polishing
paper and then with 0.3 and 0.05 µm Al$_2$O$_3$ powder
until a mirror-like surface was obtained. The electrode
was rinsed with distilled water, sonicated for 5 min in
ethanol to remove residual alumina, then the GC elec-
trode was immersed in 0.066 M phosphate buffer solu-
tion (pH 7.0) for electrochemical activation. Several
authors have addressed the electrochemical treatment
of GC electrodes [15]. Anodization of GC electrodes
forms oxygen-containing species on the electrode sur-
face. In our studies a clean GC electrode was held for
2 min at $+2.0$ V versus Ag | AgCl reference followed
by cathodic reduction at $-1.0$ V versus Ag | AgCl
reference for 2 min. At this stage the electrode turned
purple and a pair of redox peaks was developed at ca.
$-0.1$ V. The redox peaks are attributed to surface
quinone species. Longer oxidation increased the redox
peaks and the background current due to the formation
of a thick graphite oxide film. After anodic polarization
the potential was successively cycled between 1.0 and
$-1.0$ V versus Ag | AgCl reference until the cyclic
voltammogram remained constant. This treatment re-
resulted in a highly reproducible surface.

Preparation of NPQ-modified GC electrodes: NPQ
was not deposited from aqueous solution on untreated
GC even after immersion of the GC electrode for
prolonged duration in NPQ sols. Therefore, we carried
out an electrophoretic deposition procedure in order to
study the NPQ-modified GC. The oxidized GC elec-
trode was immersed in 2 mM NPQ + 1 M KCl solu-
tion. The pH was adjusted to pH 7.0 by 0.066 M
phosphate buffer. The electrode potential was cycled
continuously between 50 and $-700$ mV versus Ag | AgCl
reference.

Preparation of NPQ-modified carbon ceramic elec-
trodes (NPQ/CCEs): A mixture of 2 mM NPQ sol, 1.5
ml methanol (Frutarom, Haifa), 1.0 ml MTMOS, 0.2
ml water and 0.05 ml 11 M HCl was shaken for 2 min.
Then 1.25 g carbon powder was added and the mixture
was shaken for an additional 1 min and sonicated for 3
min. A 5 mm length of a capillary (inside diameter 1
mm) was filled with the CCE precursors and allowed to
dry overnight at ambient conditions.

2.3. Instrumentation

An EG&G PARC model 273 potentionstat with
PARC M270 software was used for steady state deposi-
tion, cyclic voltammetry (CV), and chronocoulometry
(CA) studies. Experiments were carried out in a single
compartment, three-electrode cell.
A 3-mm diameter glassy carbon rod (Atomergic Chemicals, Farmingdale, NY) sealed in a Teflon tube served as the working electrode. Pt|flag counter and Ag|AgCl | 3 M KCl reference electrodes were used. All potentials in this article are reported versus this reference electrode. Deaeration was conducted by nitrogen purging before and during the experiment.

3. Theory

3.1. Modeling of the polarization curves of redox polymer-carbon ceramic composite gas electrodes

A simplified conceptual model of the gas electrode is presented in Scheme 4 along with the notations used for the mathematical formulation of the reaction–diffusion problem. In this configuration the carbon network is held by a water permeable porous silicate network. A layer of thickness $L$ at the bottom of the electrode is uniformly flooded by the electrolyte. Oxygen from the gas phase penetrates the porous, unwetted CCE section and reaches the liquid | gas interface, where gas–liquid equilibrium prevails. The dissolved oxygen diffuses downward along the $z$ coordinate and is depleted by electrochemical reactions with reduced species ([NPQH$_2$] denoted as $c_R$) on the active polymer layer that coats the carbon grains. The reduced species are continuously regenerated by a lateral self-exchange process within the polymer along the $x$ coordinate. An electrode reaction on the surface ($x = 0$) of the carbon grains regenerates the NPQ mediator. Oxygen reacts with NPQ moieties by Eq. (1).

\[
\text{NPQH}_2 + O_2 \rightarrow \text{NPQ} + \text{H}_2\text{O}_2 \quad (1)
\]

NPQ moieties are regenerated by Eq. (2)

\[
\text{NPQ} + 2\text{H}^+ + 2e^- \rightarrow \text{NPQH}_2 \quad (2)
\]

The net reaction is a two-electron oxygen reduction process

\[
O_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \quad (3)
\]

3.1.1. Underlying assumptions

The diffusion–reaction model outlined below is based on several simplifying assumptions:

1. The oxygen reduction rate on the graphite surface is negligibly slow compared to NPQ reduction. This assumption was verified by cyclic voltammetry studies of NPQ-modified CCEs that will be outlined below.

2. The external diffusion resistance at the liquid and gas side of the active section is negligible. This assumption was confirmed by changing the gas flow rate at the backside of the electrode and stirring the solution. Both had a negligible effect on the electrode polarization curves.

3. The active thickness of the redox polymer is very small ($\ll 1 \mu\text{m}$). This assumption is justified in Section 4 based on coulometric studies of a redox NPQ–silicate coating on planar electrodes. Although all of the binder is modified by the redox moieties, most of it is in the oxidized form since the effective length for transduction of current by most redox polymers and particularly by redox silicates is rather limited.

4. Lateral ($x$ direction) oxygen gradients in the polymer film are negligible. This simplification is justified by assumption (3) and also because the diffusion coefficient of oxygen is much larger than the effective diffusion coefficient of charge transport through the redox polymer film. We shall show that the effective diffusion coefficient of the redox moieties as calculated by chronoamperometry is less than $10^{-9} \text{ cm}^2 \text{s}^{-1}$, which is approximately three orders of magnitude lower than the diffusion coefficient for dissolved oxygen.

5. The electric resistance of the electrode is of the order of a few ohms and therefore ohmic drop is negligible even for the highest current density region of the polarization curves.

6. The effective diffusion coefficients of the reduced and oxidized NPQ moieties are equal.

7. The diffusion of hydrogen ions is considered much faster than the effective diffusion of the NPQ charge carriers.

8. Oxygen reduction by naphthohydroquinone moieties follows a second-order reaction rate between dissolved oxygen and the reduced form of NPQ.

9. Dilute solutions are assumed, which can be regarded as reasonable rough approximations since an air stream feed and not pure oxygen was fed at the back of the electrode.

10. Henry’s law governs the dissolution of the oxygen near the liquid | gas boundary of the flooded electrode section.
The formulation of the mathematical problem is based on a modification of mathematical treatments [6, 16–18] which are based on differential mass balance representing reaction–diffusion schemes [19]. Unlike previous modeling this model has to account for the two-dimensional variation of the concentration profiles within the wetted section of the electrode — a variation along the z-axis due to the depletion of oxygen and along the x-axis due to the effective diffusion of charged moieties across the active redox polymer adjacent to the conductive carbon.

The governing differential equation in the x direction is given by

\[ D_R \frac{\partial^2 c_R}{\partial x^2} = K_H c_{O_2} c_R \]

(4)

where \( c_R \) and \( c_{O_2} \) are the local concentrations of (reduced NPQ) and (dissolved oxygen) moieties in the NPQ–silicate film (mol cm\(^{-2}\)). \( D_R \) is the effective diffusion coefficient (cm\(^2\) s\(^{-1}\)) for charge transport within the redox polymer. \( K_H \) is the rate coefficient of the heterogeneous bimolecular reaction between oxygen and silicate bound NPQH\(_2\) moieties which is treated as a pseudo-homogeneous reaction.

The differential equation is subject to the following boundary conditions:

\[ D_R \frac{\partial c_R}{\partial x} = k_f c_O - k_b c_R \quad \text{at} \quad x = 0 \]

(5)

\[ \frac{\partial c_R}{\partial x} = 0 \quad \text{at} \quad x = \delta \]

(6)

where \( c_O \) is the local concentration of the oxidized quinone moieties, and \( k_f \) and \( k_b \) are, respectively, the forward and backward potential-dependent Butler–Volmer coefficients given by Eqs. (7) and (8).

\[ k_f = k_{f,0} e^{(\beta n F/R)\eta} = k_{f,0} e^{B\eta} \]

(7)

\[ k_b = k_{b,0} e^{(1 - \beta n F/R)\eta} \]

(8)

where \( \eta \) is the kinetic overpotential, \( (E - E^\circ) \). \( \eta \) is negative for reduction processes. \( B = (\beta n F/R) \). The other parameters have their conventional meaning [20].

The total number of the reduced and oxidized NPQ moieties in the polymer film remains constant irrespective of position or local redox potential.

\[ c_O + c_R = c \]

(9)

According to assumption (4), \( c_{O_2} \) depends only on the vertical (z) coordinate and is invariant to the x coordinate.

The vertical variation of oxygen within the flooded section is given by a conventional steady state reaction–diffusion equation

\[ D_{O_2} \frac{\partial^2 c_{O_2}}{\partial z^2} = N \]

(10)

\[ N = n'a \left( -D_R \frac{\partial c_R}{\partial x} \right) \bigg|_{x=0} \]

(11)

where \( n' \) is the stoichiometric coefficient of the homogeneous reaction (1). For the NPQ–oxygen system \( n' = 1; \)

\( a \) is the area to volume ratio (cm\(^{-1}\)) of the carbon surface in the flooded section of the electrode. Eq. (10) is subject to the following boundary conditions at the gas liquid (\( z = 0 \)) and at the bottom of the porous layer (\( z = L \))

\[ \frac{\partial c_{O_2}}{\partial z} = 0 \quad \text{at} \quad z = L \]

(12)

\[ c_{O_2} = c_{O_2}^0 \quad \text{at} \quad z = 0 \]

(13)

where \( c_{O_2}^0 \) is oxygen solubility (mol cm\(^{-3}\)) at the liquid–gas interface of the flooded section of the electrode. \( c_{O_2}^0 \) is proportional to the partial pressure of oxygen according to Henry’s law:

\[ c_{O_2}^0 = K_b p_{O_2} \]

(14)

where, \( K_b \) is Henry’s constant and \( p_{O_2} \) is oxygen partial pressure at the gas feed.

Eqs. (4)–(13) are transformed to non-dimensional forms by the following variables

\[ C_R \equiv c_R/c \]

(15)

\[ C_{O_2} \equiv c_{O_2}/c_{O_2}^0 \]

(16)

\[ X \equiv x/\delta \]

(17)

\[ Z \equiv z/L \]

(18)

Thus, the differential equation governing charge transport in the lateral direction is

\[ \frac{\partial^2 C_R}{\partial X^2} = \alpha^2 C_{O_2} C_R \]

(19)

subject to the boundary conditions

\[ -D_R \frac{\partial C_R}{\partial X} = k_f (1 - C_R) - k_b C_R \quad \text{at} \quad X = 0 \]

(20)

\[ \frac{\partial C_R}{\partial X} = 0 \quad \text{at} \quad X = 1 \]

(21)

where \( \alpha \) is the Thiele modulus for chemical reaction in the x direction. The Thiele modulus represents the ratio between the pseudohomogeneous reaction rate of NPQH\(_2\) and dissolved oxygen and the charge diffusion rate in the polymer film.

\[ \alpha^2 = K_H C_{O_2} \left( \frac{D_R}{\delta^2} \right)^{-1} \]

(22)

The distribution of \( C_R \) versus \( X \) depends on the vertical position only due to the dependence of the oxygen concentration, \( C_{O_2} \) on the vertical coordinate.

\[ C_R = \left[ \frac{\delta k_f}{D_R x} \right] \left[ \frac{[e^{2z-x} + e^{x}]^2}{(e^{2z} - 1) + \delta (k_f + k_b) (e^{x} + 1)} \right] \]

(23)
In order to limit the number of adjustable variables in the numerical simulations we limit the following solution to large overpotentials (> 30 mV) and thus the backward reaction at the electrode can be neglected compared to the electroreduction (i.e. \( k_2 \approx k_1 \)).

The non-dimensional dependence of \( C_{O_2} \) on \( Z \) is therefore given by calculating \( dC_{O_2}/dX \) at \( X = 0 \) from Eq. (23) and substituting in Eq. (11).

\[
\frac{\partial^2 C_{O_2}}{\partial Z^2} = \frac{G}{\text{Rad} \left( \frac{1}{e^{\frac{B}{R}} + Ax C_{O_2}^{0.5} \tanh(Ax C_{O_2}^{0.5})} \right)}
\]

where the dimensionless parameters \( G \) and \( Ax \) are defined by Eqs. (25)–(28)

\[
G = \frac{n' \lambda L^2 e D_R}{\delta c_{O_2} D_{O_2}^{0.5}}
\]

\[
\text{Rad} = \frac{D_R}{k_{1,0} \delta}
\]

\[
Ax = \left[ \frac{K_{H_2O_2}^{0.5} \delta^{2.5}}{D_R} \right] = 2e^{-0.5}
\]

\[
B = \frac{\beta n F}{RT}
\]

\[
j = a L n F c k_{1,0} \left( \frac{e^{B_0}}{1 + \text{Rad} C_{O_2}^{0.5} Ax \tanh(Ax C_{O_2}^{0.5})} \right) dZ
\]

For sufficiently low overpotentials, Eq. (29) gives the Tafel dependence (electrochemical kinetic control):

\[
j = j_0 e^{B_0}
\]

\[
j_0 = an F c k_{1,0} L e
\]

The pre-exponential term, \( j_0 \), is dimensional (A cm\(^{-2}\)) and influences the absolute value of the current density but not the shape of the polarization curves.

3.1.2. Dynamic solution

The time-dependent response of the electrode is solved by assuming that the relaxation time of the polymeric film (\( \tau_x = aD_R/\delta \)) is much faster compared to the relaxation time corresponding to the vertical variation of dissolved oxygen \( (D_{O_2}/L^2) \). This condition is guaranteed for large \( G(c/e_{O_2}^{0.5}) \). We have shown in Section 4 that indeed \( G \gg 1 \) for the NPQ-modified carbon ceramic composite electrode. The dynamic form of Eq. (24) is given by

\[
\frac{\partial C_{O_2}}{\partial \tau_x} = \frac{\partial^2 C_{O_2}}{\partial Z^2} \left( \frac{G}{\text{Rad} \left( \frac{1}{e^{\frac{B}{R}} + Ax C_{O_2}^{0.5} \tanh(Ax C_{O_2}^{0.5})} \right)} \right)
\]

where

\[
\tau_x = \frac{D_{O_2} t}{L^2}
\]

3.1.3. Numerical solution

Eq. (28) was solved by a finite difference scheme. The solution involves three lumped non-dimensional parameters in addition to \( j_0 \), which, however, does not influence the shape of the curves. \( Ax \), \( G \) and the Damkohler number (\( \text{Rad} \exp(B_0) \)) determine the rate controlling step for oxygen reduction. For low overvoltage (i.e. small Damkohler number) the current is always controlled by the rate of the electrochemical charge transfer. In these cases the current follows an exponential dependence on the overpotential, \( \eta \). For low \( G \) and high overvoltage the current is controlled by the rate of the homogeneous reaction between the dissolved oxygen and NPQH\(_2\) moieties. For large \( G \) and high overvoltage the current is controlled by the rate of charge transport across the redox polymer film.

The dependence of the polarization curves on \( Ax \), \( G \) and \( \text{Rad} \) is illustrated in Figs. 1–3 for \( j_0 = 5.78 \times 10^{-8} \) mA cm\(^{-2}\). In order to minimize the number of figures we demonstrate only the dependence of the shape of the polarization curves around a set of parameters that characterizes the experimental steady state polarization curves of the NPQ composite electrodes in these studies.

Fig. 1 describes the dependence of the polarization curves for \( G = 20 \) and \( \text{Rad} = 10^5 \) on \( Ax \), the lateral Thiele modulus. For the low overpotential range, the rate of oxygen reduction obeys Tafel-like behavior irrespective of \( Ax \). At higher potentials, \( Ax \) determines the deviation of the simulated curves from electrochemical kinetics control. Higher \( Ax \) electrodes are favorable, exhibiting larger attainable current densities. Indeed, the oxygen concentration profile at low overvoltage is characterized by uniform concentrations, \( C_{O_2} \approx 1 \) and \( C_{O_2} = 1 \) (\( \eta = -200 \) mV, Fig. 1, insert A). For high overvoltage and low \( Ax \) conditions the homogeneous kinetics are the rate-limiting step and thus both oxygen and NPQH\(_2\) are available throughout the electrode (\( \eta = -700 \) mV and \( Ax = 1 \), inserts B and C). Thus availability of NPQ at the electrode surface becomes a limiting factor.
Fig. 2 depicts the dependence of the simulated polarization curves for $G = 20$ and $Ax = 100$ on $Rad$. As for Fig. 1 the different curves approach the Tafel kinetics at low overpotentials. The shift from a Tafel shape occurs at higher overpotentials for larger values of $Rad$. Larger diffusion coefficients of the charge transfer moieties in the redox polymer (i.e. larger $Rad$, Eq. (26)) favor higher limiting currents. The insets in Fig. 2 demonstrate the evolution of the limiting factor under low and high overvoltages. For low overvoltage both oxygen and NPQ are available throughout the active section of the electrode (inset A). At high overvoltages insets B and C show that oxygen supply becomes the limiting factor.

Fig. 3 depicts the dependence of the polarization curves on $G$ ($Rad = 10^5$ and $Ax = 100$). For low overpotentials the current density still obeys an exponential Tafel dependence on the applied potential. Under these conditions both NPQ ($C_Q = 1 - C_R$) and oxygen ($C_{O_2}$) are available throughout the active portion of the electrode (inset A). However, for high overpotentials availability of oxygen becomes the limiting factor for the high-$G$ conditions (lower curve in inset B) while for low-$G$ conditions ($G = 0.02$) oxygen is available almost throughout the active zone and availability of NPQH$_2$ limits oxygen conversion (inset C).

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**Fig. 1.** Simulated polarization curves for $G = 20$, $Rad = 10^5$ and various $Ax$ parameters. Insert A: Oxygen concentration profiles for $Ax = 1$ and $Ax = 1000$ for $\eta = -200$ mV vs Ag/AgCl. Insert B: Oxygen concentration profiles for $Ax = 1$ and $Ax = 1000$ for $\eta = -700$ mV vs Ag/AgCl. Insert C: NPQH$_2$ profile as a function of the lateral position in the active redox film at $Ax = 1$, $\eta = -700$ mV vs Ag/AgCl and $Z = 0.2$ and 0.8.

**Fig. 2.** Simulated polarization curves for $G = 20$, $Ax = 100$ and different $Rad$ parameters. Insert A: Oxygen concentration profiles for $Rad = 100$ and $10^5$ for $\eta = -100$ mV vs Ag/AgCl. Insert B: Oxygen concentration profiles for $Rad = 100$ and $10^5$ for $\eta = -700$ mV vs Ag/AgCl. Insert C: NPQ profile as a function of the lateral position in the active redox film at $Rad = 10^5$, $\eta = -700$ mV vs Ag/AgCl and $Z = 0.2$ and 0.8.
4. Experimental results

The first part in the development of the porous redox electrode involved characterization of the redox polymer. Since NPQ was never studied on carbon electrodes we deposited a polymer film on a GC electrode and studied its characteristics.

4.1. Characterization of NPQ-coated electrodes

Conventional dip coating of NPQ–silicate film failed to produce stable silicate films on glassy carbon electrodes. Therefore, we resorted to electrophoretic deposition of the silicate film. Electrophoretic deposition of the silicate coating was carried out by repeated cycling of the electrode potential at 2 mM NPQ, 1 M KCl which was set to pH 7.0 by 0.066 M phosphate buffer. The scan rate was 20 mV s$^{-1}$. These conditions produced the fastest polymerization rate. Fig. 4 describes the evolution of the CV curves as a function of the duration of the NPQ electrophoretic deposition. The inset of Fig. 4 depicts the anodic charge as a function of the number of cycles calculated from the integral of the anodic CV peak. Saturation of the deposit takes place at approximately 1.55 mC cm$^{-2}$ which corresponds to $7.8 \times 10^{-5}$ mol NPQ cm$^{-2}$. Taking full coverage to be $10^{-10}$ mol cm$^{-2}$ Ref. [21] implies that saturation is achieved for ca 78 NPQ layers. Further, assuming that the thickness of each layer is 2 nm gives 0.155 nm film thickness. These rough calculations show that even under optimal polymerization conditions the electroactive film thickness for the NPQ–silicate is very small. These results support assumption (3) in Section 3.

Fig. 5 depicts a typical chronoamperometric curve for an NPQ–silicate film on a GC electrode. The CA was conducted in 1 M KCl + 0.066 M phosphate buffer pH 7.0, potential step from 0 to $-0.6$ V versus Ag | AgCl. The film had an anodic charge of 1.50 mC cm$^{-2}$ (as of Fig. 4 after 100 cycles) The curve shows linear dependence of the current density on $t^{-0.5}$ at short times. The product $D_R c^0.5$ can be calculated according to the Cottrel equation [20] to be $10^{-6}$ mol s$^{-0.5}$ cm$^{-2}$, $c$ is not known, but assuming $c \sim 5$ mM one obtains $D_R = 4.0 \times 10^{-8}$ cm$^2$ s$^{-1}$ which is a relatively high diffusion coefficient for redox polymers.

Fig. 3. Simulated polarization curves for $A_x = 100$, Rad = $10^5$ and various $G$ parameters. Insert A: Oxygen concentration profiles for $G = 0.02$ and 200 for $\eta = 200$ mV vs Ag | AgCl; Insert B: Oxygen concentration profiles for $G = 0.02$ and 200 for $\eta = 700$ mV vs Ag | AgCl. Insert C: NPQ profile as a function of the lateral position in the active redox film at $G = 0.02$, $\eta = 700$ mV vs Ag | AgCl and $Z = 0.2$ and 0.8.

Fig. 4. Evolution of CV curves as a function of NPQ deposition time. Deposition was carried out by cycling the electrode potential between $+100$ and $-750$ mV vs Ag | AgCl in 1 M KCl, 0.066 M phosphate buffer, pH 7.0, 2.2 mM NPQ. Scan rate = 20 mV s$^{-1}$. CV curves were measured in 1 M KCl, 0.066 M phosphate buffer pH 7.0, scan rate = 20 mV s$^{-1}$. The curves were taken after 10, 20, 30, 50 and 100 deposition cycles. Inset. Accumulated charge corresponding to the cathodic peak as a function of the number of deposition cycles.
Fig. 5. Typical chronoamperometric curves for an NPQ film that was deposited on GC electrode according to the protocol of Fig. 4. Hundred deposition cycles were used. The test was conducted in deaerated 1 M KCl, 0.066 M phosphate buffer pH 7.0; the potential was stepped from 0 to −600 mV vs Ag | AgCl reference electrode.

Figs. 6A and B and 7A and B compare the cyclic voltammetry of NPQ-modified CCE and GC electrodes and the corresponding peak potentials versus pH. The cyclic voltammetry tests were carried out under identical conditions using 0.066 mM phosphate buffer adjusted to the required pH by KOH or HCl solutions. In all cases 1 M KCl supporting electrolytes was added and the solution was deaerated with nitrogen. In the case of the NPQ/CCE electrode, a nitrogen (99.99%) stream was fed at the back of the electrode to prevent oxygen penetration. The cyclic voltammetry curves show that the two NPQ-modified electrodes maintain approximately the same formal potentials and all other pertinent characteristics of naphthoquinone. The anodic and cathodic peak separation of the CCE is somewhat larger compared to the surface confined electrodes due to the more heterogeneous nature of these electrodes and the larger thickness of their wetted section. Fig. 7A and B shows that the anodic and cathodic peak potentials of the modified CCE and GC electrodes are 55 and 57 mV decade⁻¹, respectively, for pH < 7.5. The deviation from the expected 59 mV decade⁻¹ is explained by the relatively high scan rate (100 mV s⁻¹) employed in this study which induced a somewhat wider peak separation and a corresponding uncertainty.

Fig. 6. (A) Cyclic voltammetry of NPQ-modified CCEs in deaerated 1 M KCl + 0.066 M phosphate buffer solution. Nitrogen was passed at the top of the electrode. (B) CV of GC electrode in 2 mM NPQ in 1 M KCl + 0.066 M phosphate buffer. Scan rate = 100 mV s⁻¹. The pH was corrected by addition of KOH or HCl solutions.

Fig. 7. pH dependence of the positive and negative peak potentials and the formal potential of NPQ-modified CCEs (A) and GC in 2 mM NPQ solution (B). Experimental conditions are identical to Fig. 6.
in determining the formal potential. The slope changes at pH 7.5 due to the deprotonation of the hydroquinone, and the slope of the formal potential becomes roughly half of the low pH region (29 and 34 for CCE and GC, respectively). This is expected for redox reactions involving exchange of two electrons and one proton [21].

4.2. Oxygen reduction on NPQ/CCE

Oxygen reduction on NPQ/CCE was investigated by exposing the backside of the test electrodes to air. Fig. 8 depicts CV studies of oxygen reduction on different compositions of NPQ/CCEs as compared to CV scans with nitrogen flow at the backside of the electrodes. For all the electrodes tested the molar concentration of Si in the precursors was kept constant but the ratio between NPQ and MTMOS was varied. Three trends can be observed in the set of CV curves of Fig. 8: (1). Increased catalytic activity towards oxygen reduction is clearly observed for all the NPQ/CCE electrodes. This activity is increased as the ratio between NPQ and MTMOS is increased. (2) The onset of oxygen reduction shifts from approximately −550 mV versus Ag | AgCl reference for the NPQ-free blank electrode to approximately −300 mV for NPQ:MTMOS < 10. E = −300 mV corresponds to the formal potential of NPQ at pH 7.0. Increasing the ratio between NPQ and MTMOS above approximately 1:10 did not induce a further positive shift of the onset of the catalytic reduction wave. This is to be expected since the catalytic activity relies on the electroreduction of NPQH₂ at the carbon surface, which becomes exceedingly slow at potentials that are more negative than the formal potential of NPQ/NPQH₂. (3) The background current for the nitrogen feed as well as for air fed electrodes increased when the ratio between NPQ and MTMOS was increased. This phenomenon is not related to the
catalytic activity because the background current was identical for the air and nitrogen-fed electrodes. The decrease of the background current is attributed to increased hydrophobicity due to the increased coverage of the CCE by methyl silicate surface groups. As similar decrease of electrode wettability was reported for methyltrimethoxysilane/tetramethoxysilane-derived sol–gel networks [22,23].

Fig. 9 shows the observed capacitance of the CCEs versus the molar ratio of MTMOS:NPQ. The observed capacitance increases as the relative concentration of NPQ in the silicate binder is increased. This is attributed to the hydrophilic nature of NPQ, which results in better wettability. The observed capacitance of these electrodes can be calculated by

\[
C_{obs} = (j_a + j_c)_{at} - 50 \text{ mV} / v
\]  

(34)

where \(j_a\) and \(j_c\) are the absolute values of the anodic and cathodic background current densities, and \(v\) is the scan rate. This dependence is used for the simulation of the CCE polarization curves.

Fig. 10 depicts four polarization curves that were recorded on NPQ-modified CCEs. In all cases the tests were conducted for air feed (21% oxygen), in 1 M KCl + 0.066 M phosphate buffer pH 7.0 deaerated by N\(_2\) bubbling. The curves correspond to 3.3, 10, 33 and

\[
E / \text{mV vs Ag|AgCl}
\]  

Fig. 8. (Continued)
Fig. 10. Simulated (symbols) and experimental steady state polarization curves for four different NPQ:MTMOS-modified CCEs exposed to air at the backside of the electrode. The curves correspond to NPQ:MTMOS ratio = 3.3, 10, 33 and 100. Solution: 1 M KCl, 0.066 mM phosphate buffer. Simulation parameters Rad = 1.2 × 10^4, \( Ax = 110 \), flooded thickness \( L = 200, 150, 87 \) and 50 \( \mu m \).

**Table 1** Simulation results (\( Ax = 110 \), Rad = 1.2 × 10^4, \( K_{j\theta} = 1.36 \times 10^{-10} \), \( K_G = 3.87 \times 10^{-5} \))

<table>
<thead>
<tr>
<th>r, MTMOS:NPQ molar ratio</th>
<th>( C_{obs}/\mu F cm^{-2} )</th>
<th>( G/A cm^{-2} )</th>
<th>( j_0/A cm^{-2} )</th>
<th>( L/\mu m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>1400</td>
<td>23</td>
<td>5.78 × 10^{-8}</td>
<td>200</td>
</tr>
<tr>
<td>10</td>
<td>1050</td>
<td>4.3</td>
<td>1.44 × 10^{-9}</td>
<td>150</td>
</tr>
<tr>
<td>33</td>
<td>600</td>
<td>0.42</td>
<td>2.47 × 10^{-9}</td>
<td>86</td>
</tr>
<tr>
<td>100</td>
<td>350</td>
<td>0.048</td>
<td>4.8 × 10^{-10}</td>
<td>50</td>
</tr>
</tbody>
</table>

\( *L \) was calculated for \( n' = 1, \ c = 10^{-6} M cm^{-3}, c_{O_2}^o = 3 \times 10^{-7} M cm^{-3}, D_R = 10^{-8} cm^2 s^{-1}, D_{O_2} = 6 \times 10^{-6} cm^2 s^{-1}, \delta = 10^{-5} cm. \)

Fig. 11. Dynamic response of NPQ/CCE electrodes (MTMOS:NPQ = 3.3) exposed to different oxygen partial pressures. The electrodes are placed in a deaerated solution, containing 1 M KCl + 0.066 mM phosphate buffer pH 7.0.

100 MTMOS:NPQ molar ratio. Steady-state polarization curves were recorded at 0.5 mV s^{-1} scan rate. Thus, the four lines represent four different thicknesses of the wetted section of the CCE electrodes. The polarization curves were fitted to the model predictions using the same \( Ax \) and Rad but changing \( G \) and \( j_0 \). However, \( G \) and \( j_0 \) for the different electrodes were not free parameters since they both depend on the MTMOS:NPQ ratio, \( r \). \( G \) is proportional to \( L^2c \) and \( j_0 \) is proportional to \( Lc \). \( c \) is proportional to the MTMOS:NPQ ratio. \( L \) is assumed to be proportional to the specific surface area of the carbon, which is in turn proportional to the observed capacitance of the electrodes.

\[
j_0 = K_{j\theta} C_{obs} / r
\]

\[
G = K_G c_{obs}^2 / r
\]

Therefore, the best fit of all the four polarization curves was performed with two free parameters \( K_{j\theta} \) and \( K_G \). Table 1 summarizes the best-fit parameters. In addition, assuming constant \( c \) and \( \delta \), one can obtain an approximate value for the thickness of the wetted layer of the four electrodes \( L \). A four-fold decrease in the active wetted layer thickness was observed when the NPQ loading was changed from \( r = 3.3 \) to 100.

Fig. 11 depicts the dependence of the NPQ/CCE response on oxygen partial pressure at the gas above the electrode. In these studies we used an MTMOS:NPQ molar ratio of 3 operated at an overvoltage of −500 mV, in 1 M KCl and 0.066 M phosphate buffer in deaerated solution. The experimental observations were compared to simulated results based on the best-fit parameters of Fig. 10. The observed current–concentration dependence show a reasonably good fit to the predicted curve, at least for the low concentration range where the model assumptions hold.

4.3. Dynamic response

The proposed electrode can be used as a gas sensor. Fig. 12 depicts the dynamic response of NPQ-modified CCE electrode to a series of step changes of oxygen concentration at the back of the electrode. CCEs with MTMOS:NPQ = 3.3 were tested in 1 M KCl and 0.066 M phosphate buffer in deaerated solution. The experimental observations were compared to simulated results based on the best-fit parameters of Fig. 10. The observed current–concentration dependence show a reasonably good fit to the predicted curve, at least for the low concentration range where the model assumptions hold.

Fig. 12. Simulated and experimental oxygen calibration curves of NPQ/CCE. Experimental conditions and simulation parameters are identical to the best fit obtained in the simulation of Fig. 11.
M phosphate buffer deaerated solution at \( \eta = -500 \) mV. The electrode response was reproducible and the response time for a concentration increase was approximately 60 s. The response to a step change decrease in concentration was about 1.5 times larger, as compared to an upward step change.

In order to explain the asymmetric time response to upward and downward step changes we simulated the current–time response for the upward and downward step changes of oxygen concentration from 47 to 21%. These curves are shown in a normalized form in Fig. 13 as compared to the experimental curves. Both experimental and simulated results give faster response for increasing oxygen partial pressure step than for decreasing step changes, due to a faster reaction rate at higher concentrations.

5. Concluding remarks

This paper presents an unconventional form of gas electrode where a pseudo-homogeneous charge transfer step precedes the diffusion and the electrochemical charge transfer steps. Mathematical formulation of the problem shows that the performance of these electrodes depends, to a large extent, on the rate of the homogenous reaction kinetics and on the charge transport rate within the polymer film. Each of these steps can constitute the limiting step under some operating conditions. Oxygen reduction on NPQ/CCEs was examined and its performance was used to examine the validity of the theoretical predictions. The experimental observations fitted the theory rather well and diffusion limitation was encountered at high overpotentials.

6. Notation

- \( a \) Specific surface area of the wetted carbon in NPQ/CCE (cm\(^{-1}\))
- \( AX \) Defined in Eq. (27)
- \( B \) Tafel slope (V/decade)
- \( c \) Sum of NPQ and NPQH\(_2\) concentrations in the NPQ film (mol cm\(^{-3}\))
- \( c_R \) NPQH\(_2\) concentration in the NPQ film (mol cm\(^{-3}\))
- \( c_0 \) NPQ concentration in the NPQ film (mol cm\(^{-3}\))
- \( C_{Rk} \) Dimensionless NPQH\(_2\) concentration (\( c_{Rk} / c \))
- \( C_{Qk} \) Dimensionless NPQ concentration (\( c_{Qk} / c \))
- \( c_O^0 \) Dissolved oxygen concentration in equilibrium with the gas feed (mol cm\(^{-3}\))
- \( C_{O2} \) Dimensionless oxygen concentration in the active part of NPQ/CCE (\( c_{O2} / c_O^0 \))
- \( C_{obs} \) Observed specific capacitance of NPQ-modified CCE (F cm\(^{-2}\))
- \( D_{O2} \) Oxygen diffusion coefficient in an electrolyte (cm\(^2\) s\(^{-1}\))
- \( D_R \) Effective diffusion coefficient for charge transport within the redox polymer (cm\(^2\) s\(^{-1}\))
- \( E \) Electrode potential versus Ag\mid AgCl reference electrode (V)
- \( F \) Faraday constant (C mol\(^{-1}\))
- \( G \) Dimensionless parameter, defined in Eq. (25)
- \( j \) Current density (A cm\(^{-2}\))
- \( j_0 \) Current density under kinetic control conditions (Tafel region) (A cm\(^{-2}\))
- \( K_{Qk} \) Defined by Eq. (36)
- \( K_{H} \) Kinetic coefficient of the pseudohomogenous rate of oxygen reduction (cm s\(^{-1}\))
- \( K_h \) Henry’s constant
- \( K_{Q0} \) Defined by Eq. (35)
- \( k_{f} \) Potential-dependent cathodic kinetic coefficient (cm s\(^{-1}\))
- \( k_{f0} \) Potential-dependent cathodic kinetic coefficient at \( \eta = 0 \) (cm s\(^{-1}\))
- \( L \) Thickness of the active section of the electrode (cm)
- \( n \) The number of exchanged electrons in the electrochemical reaction
- \( n' \) The stoichiometric coefficient of NPQH\(_2\) in the chemical reduction of oxygen
- \( N \) Oxygen transfer rate per unit electrode volume (mol s\(^{-1}\) cm\(^{-3}\))
- \( pO_2 \) Oxygen partial pressure (bar)
- \( r \) MTMOS-NPQ molar ratio
- \( \text{Rad} \) Defined by Eq. (26)
- \( \chi \) Lateral coordinate (cm)
- \( \chi \) Dimensionless lateral coordinate (\( \chi / \delta \))
- \( z \) Vertical coordinate (cm)
- \( Z \) Dimensionless vertical coordinate (\( z / L \))
- \( \delta \) Thiele modulus in the lateral direction

Fig. 13. Normalized asymmetric dynamic response of a CCE electrode (MTMOS:NPQ molar ratio = 3.3) to oxygen concentration step changes from 47 to 21% and from 10 to 68% in deaerated 1 M KCl + 0.066 M phosphate buffer pH 7.0 solution. Solid lines correspond to simulated curves and symbols correspond to experimental observations.
η  \( E - E^\circ \), overvoltage (V)

τ  Dimensionless time, defined in Eq. (32)

δ  Effective thickness of the active NPQ film (cm)

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References