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Kinetic models for detection of toxicity in a microbial fuel cell based biosensor

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ABSTRACT

Currently available models describing microbial fuel cell (MFC) polarization curves, do not describe the effect of the presence of toxic components. A bioelectrochemical model combined with enzyme inhibition kinetics, that describes the polarization curve of an MFC-based biosensor, was modified to describe four types of toxicity. To get a stable and sensitive sensor, the overpotential has to be controlled. Simulations with the four modified models were performed to predict the overpotential that gives the most sensitive sensor. These simulations were based on data and parameter values from experimental results under non-toxic conditions. Given the parameter values from experimental results, controlling the overpotential at 250 mV leads to a sensor that is most sensitive to components that influence the whole bacterial metabolism or that influence the substrate affinity constant (Km). Controlling the overpotential at 105 mV is the most sensitive setting for components influencing the ratio of biochemical over electrochemical reaction rate constants ($K1$), while an overpotential of 76 mV gives the most sensitive setting for components that influence the ratio of the forward over backward biochemical rate constants ($K2$).

The sensitivity of the biosensor was also analyzed for robustness against changes in the model parameters other than toxicity. As an example, the tradeoff between sensitivity and robustness for the model describing changes on $K1$ ($IK1$) is presented. The biosensor is sensitive for toxic components and robust for changes in model parameter $K2$ when overpotential is controlled between 118 and 140 mV under the simulated conditions.

1. Introduction

Water quality is an important factor that water companies need to monitor. Many methods are used to monitor the chemical components that determine water quality. To measure chemical components, both on-line and offline sensors are available. A drawback of most off-line sensors is, amongst others, that detection takes several hours or even days. Hence this type of sensor is, in general, unsuitable for alarming and process control. Furthermore, these sensors are very accurate for some components but not at all for others. Therefore online, generic sensors are needed as well, especially for real-time applications. In addition to physical–chemical sensors, biosensors like fish, daphnia and bacterial sensors are available. These sensors are sensitive to many components and placed online in systems. They need, however, nonlinear transducers to convert the signal of organisms into a signal that can be read by operators, are costly and need a lot of maintenance (Grieshaber et al., 2008; Kim et al., 2005; Stein et al., 2010; Vanrolleghem, 1994; Hasan et al., 2005; Willemsen et al., 1995). A microbial fuel cell (MFC)-based biosensor was therefore proposed as a direct biosensor for toxicity (Kim et al., 2005; Stein et al., 2010).

A microbial fuel cell is a device in which a chemical signal is converted into an electrical signal. Microorganisms convert organic substrate into carbon dioxide, protons and electrons. Microorganisms use an anode as their electron acceptor when no soluble electron acceptor is present. Electrons flow from the anode to the cathode where e.g. oxygen is reduced. The flow of electrons is measured as current. This current is a linear measure of the activity of microorganisms. When a toxic component passes the microorganisms, their activity will change, most likely decrease. Hence, fewer electrons are transported and current then decreases as well. In this way, a microbial fuel cell-based biosensor provides a direct measure for water quality (Kim et al., 2005; Logan et al., 2006).

Activity of microorganisms depends on temperature and pH. Hence to get an accurate signal from the MFC-based biosensor, pH and temperature need to be controlled or they should be measured and corrected for in a signal processing step. The activity of microorganisms also depends on the energy obtained from consumption of substrate. The energy related to the release of electrons at the anode depends on the difference between prevailing anode poten-

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tial and equilibrium anode potential at zero-current. This potential difference is called overpotential. The overpotential needs to be controlled to get a stable baseline under nontoxic conditions. However, it was not yet investigated at which overpotential the sensor is most sensitive for detection of toxic components.

The objective of this paper is to offer a methodology how to evaluate at which overpotential the sensor is most sensitive to toxic components.

One has to realize that current is not only determined by the overpotential, but also by other environmental factors such as the substrate concentration. Ideally, changes in e.g. substrate concentration during measurement should not influence the detection of toxic components. The sensitivity of the sensor for toxic components should not decrease when environmental parameters like substrate concentration change. In addition to a high sensitivity with respect to toxic components, the sensor thus also needs to be robust against changes in environmental parameters.

The approach to find an overpotential, at which the sensor is sensitive to toxic components and robust against environmental disturbances, was to use a model that describes current production in microbial fuel cells. There are several models that describe polarization curves (Finkelstein et al., 2006; Hamelers et al., 2011; Marcus et al., 2007; Picioreanu et al., 2007, 2008; Torres et al., 2008). The starting point for the analysis here is the Butler–Volmer–Monod (BVM) model as presented by Hamelers et al. (2011). It is given by

$$I = I_{\max} \frac{1 - e^{-\eta \cdot f}}{K1 \cdot e^{-(1-\alpha)\cdot\eta\cdot f} + K2 \cdot e^{-\eta \cdot f} + (Km/S) + 1} \quad (1)$$

where $I_{\max}$ (mA) is the maximum current determined by maximum enzymatic rates of microorganisms, η is the overpotential (V), $K1$ is a lumped parameter describing the ratio between biochemical and electrochemical rate constants, $K2$ is a lumped parameter describing the forward over backward biochemical rate constants, Km (mol/l) is substrate affinity constant and S (mol/l) substrate concentration. Furthermore, $f = F/RT$ with F Faraday's constant, R the gas constant and T the temperature. This model is based on a representation of the underlying biochemical conversions and electron transfer reactions that take place on the anode. Hence, it contains a combination of enzyme kinetics and electrochemical kinetics. The kinetic scheme is presented in Fig. 1.

As yet, this model does not contain any term that accounts for the presence of inhibiting components. Hence, in this paper, for the purpose of toxicity detection, the model is extended with an inhibition term. Next, the sensitivity of the sensor for toxic components as a function of overpotential will be examined. Through simulations it will be investigated how the mode of action of the toxic component influences the change in current when a toxic component is present. Then, it will be determined at which overpotential this change is the largest and thus the sensor is the most sensitive. This gives the optimal overpotential at which the sensor needs to be controlled under non-toxic conditions. In addition to this, a parameter sensitivity analysis is conducted to investigate the robustness of the sensor and to investigate how the choice of overpotential is influenced by the parameter values in (1).

2. Methods

As a starting point the model (1), as introduced by Hamelers et al. (2011), is used. The assumption is that the effect of toxicity can be described and modeled via an effect on the kinetic reaction rates involved in electron transfer. Depending on the mechanisms how the cell is influenced by the component there are several reaction rates that can be influenced by a toxic component. Four models are proposed, containing an inhibition term in which χi is the concentration of toxic component (mmol/l) and Ki the affinity constant (mmol/l). A smaller Ki implies that the component is more toxic to the microorganism.

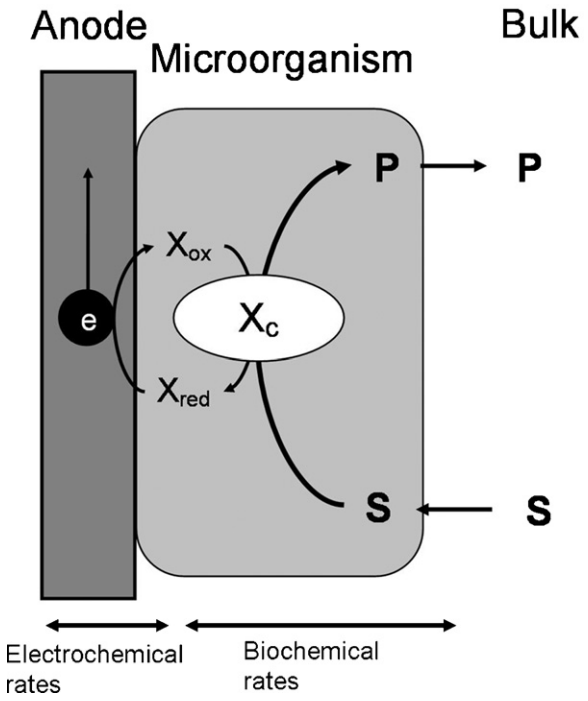

Fig. 1. Kinetic scheme of the bio-anode. Substrate (S) from the bulk phase diffuses in to the cell and is converted by an enzymatic reaction to form the redox component complex X_C in the micro-organism. This biochemical conversion leads to products (P) that diffuse to the bulk phase again. Electrons that are released in the conversion are transported to the electrode via a redox component (X_{ox}/X_{red}). Adapted from Hamelers et al. (2011).

(1) In the first model it is assumed that the toxic component acts as a noncompetitive inhibitor or as an irreversible inhibitor (Bisswanger, 2008). Consequently, the model is given by:

$$I = I_{\max} \frac{1 - e^{-\eta \cdot f}}{K1 \cdot e^{-(1-\alpha)\cdot\eta\cdot f} + K2 \cdot e^{-\eta \cdot f} + (Km/S) + 1} \cdot \frac{Ki}{Ki + \chi i} \quad (2)$$

This model is referred to as "Itox".

(2) Parameter $K1$ describes the ratio between biochemical and electrochemical reaction rate constants. This ratio may change when toxic components can act as electron acceptors. In this case the redox complex is not fully oxidized at the anode but partly at the toxic component and hence current decreases. The model for this case is given by:

$$I = I_{\max} \frac{1 - e^{-\eta \cdot f}}{K1 \cdot ((Ki + \chi i)/Ki) \cdot e^{-(1-\alpha)\cdot\eta\cdot f} + K2 \cdot e^{-\eta \cdot f} + (Km/S) + 1} \quad (3)$$

This model is referred to as "IK1".

(3) Parameter $K2$ describes the ratio between the forward and backward reaction rate constants of substrate oxidation. This ratio can change when no product is formed anymore or much more product (protons and CO_2) is formed. The ratio also changes when the toxic component is an acid. The increased proton concentration leads to a reduction of the forward

Table 1
Parameter values used in the simulations.

Parameter	Value	Unit
$K1$	1	–
$K2$	15	–
α	0.5	–
I_{max}	2	mA
Km	0.1	mmol/l
S	5	mmol/l
f	0.0383	
Ki	1	mmol/l
χi	0.1 or 2.0	mmol/l

reaction rate.

$$I = I_{max}\frac{1 - e^{-\eta \cdot f}}{K1 \cdot e^{-(1-\alpha)\cdot\eta\cdot f} + K2 \cdot ((Ki + \chi i)/Ki) \cdot e^{-\eta \cdot f} + (Km/S) + 1} \quad (4)$$

This model is referred to as "IK2".

(4) The substrate affinity constant Km may change when there is a competition between substrate and toxic component to bind to the redox complex (Bisswanger, 2008).

$$I = I_{max}\frac{1 - e^{-\eta \cdot f}}{K1 \cdot e^{-(1-\alpha)\cdot\eta\cdot f} + K2 \cdot e^{-\eta \cdot f} + (Km/S)((Ki + \chi i)/Ki) + 1} \quad (5)$$

This model is referred to as "IKm".

As noticed before, the Butler–Volmer–Monod model is based on enzyme and electrochemical kinetics. The proposed models can, therefore, only describe kinetic inhibition of microorganisms and do not describe the various mechanisms of toxic effects on the cell (Bock Gu and Cheol Gil, 2001; Lee, 2006). Consequently, from the results it is most likely not possible to tell if the toxic component is e.g. a DNA damaging agent or a protein damaging agent or is damaging otherwise.

In previous studies several polarization curves were made under non-toxic conditions. From these curves values for model parameters $K1$, $K2$ and α were calculated by Hamelers et al. (2011). Similar values as those presented by Hamelers et al. (2011) were used for the simulations in this paper. In addition to this, values of parameters I_{max}, Km and S were estimated from earlier experiments (unpublished). Table 1 summarizes parameter values used in the simulations. The overpotential was taken between −50 mV and 250 mV.

For the simulations, no explicit component was chosen. Therefore there is no concentration known, nor a value of Ki. As the inhibition term $Ki/(Ki + \chi i)$ determines the value of $dI/d\chi i$ and thus the value of the overpotential at which $dI/d\chi i$ is maximal, it is important to cover a wide range between the possible extreme values 0 and 1. The values used in the simulations are: $Ki = 1$ mmol/l, $\chi i = 0.1$ mmol/l or 2 mmol/l, thus achieving that the inhibition term is 0.9 and 0.33, respectively.

3. Results

3.1. Current

For each of the four proposed models the electrical current is simulated as a function of the anodic overpotential. As a reference, the results of the BVM-model (Eq. (1)) indicated as I, are also presented. From Fig. 2 it can be observed that sigmoidal curves result. Compared to the response under non-toxic conditions (fat line) the slope of the curve at the inflection point and final current at high overpotential can be different. From the response of model Itox (dotted line) it can be seen that both the slope and maximum are smaller. This is in line with what is expected, as in this model the inhibition term influences the complete current at all overpotentials. Model IK1 (solid line) also shows a decreased slope but the final current seems to approach the same maximum current as under non-toxic conditions. The slope in model IK2 (large dashed line) is similar to the slope of the non-toxic condition and also the maximum current reached is equal. The graph is only shifted to higher overpotentials (to the right). Model IKm (small dash) shows a slightly lower slope but mainly the maximum is lowered when a toxic component is present.

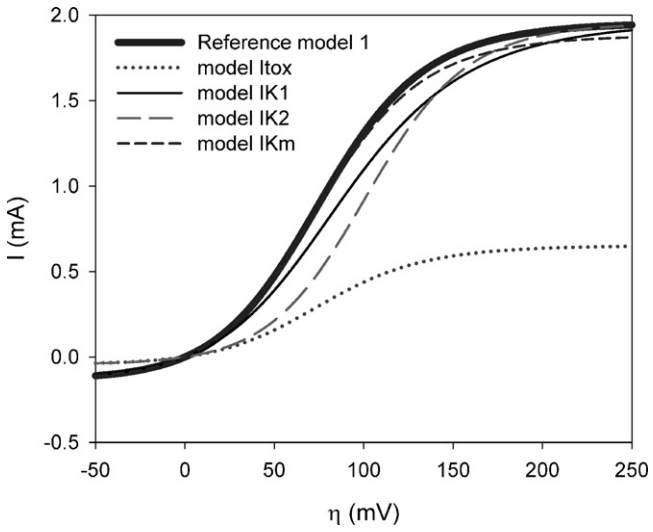

Fig. 2. polarization curves for all four models (Eqs. (2)–(5)) (with $\chi i = 2$, $Ki = 1$) and the reference model (Eq. (1)).

From these simulated curves it can be observed that, depending on the mode of action of the toxic component, the difference between toxic and non-toxic is significantly influenced by the chosen overpotential set point.

The results in Fig. 2 suggest that by measuring the polarization curve under non-toxic conditions and for any specific toxic substance under toxic conditions it would be possible to discriminate between the four alternative inhibition mechanisms.

3.2. Sensitivity for toxic components

The biosensor will be most sensitive for toxic components when the change in current is the highest for the same change in concentration of toxic component. This implies that the derivative of the current with respect to the concentration of toxic component, which is a function of η, should be maximal. Consequently, the goal is to find

$$\eta^* = arg \max_{\eta \in [-50,250]} \frac{dI(\eta)}{d\chi i} \quad (6)$$

where $dI(\eta)/d\chi i$ is the sensitivity of the current for toxic components and η^* is the overpotential that gives maximum sensitivity on the interval [−50, 250] mV.

In Fig. 3 the derivative of current to toxicity, $dI/d\chi i$, is plotted as a function of overpotential, η. When $dI/d\chi i$ is at its maximum value, the sensor is most sensitive at this overpotential. From this figure it is observed that model Itox (dotted) and IKm (small dash) are most sensitive when overpotential is as high as possible, in this case 250 mV. Model IK1 and IK2 have their maximum at lower overpotentials. Values of the optimal overpotential, η^*, are shown in Table 2 for a toxicity concentration of 2 mmol/l and 0.1 mmol/l

Table 2
Overpotentials at which the change of current due to toxicity is maximal.

Model	$\chi i = 2$ mM		$\chi i = 0.1$ mM	
	Overpotential η (mV)	$dI/d\chi i$ (mA l/mmol)	Overpotential η (mV)	$dI/d\chi i$ (mA l/mmol)
Itox	250	0.20	250	1.60
IK1	112	0.09	105	0.13
IK2	100	0.14	76	0.33
IKm	250	0.03	250	0.04

calculated with the given parameter values from Table 1. Hence, depending on the mechanisms of toxicity for the microorganisms, the optimum overpotential for control of the sensor is different.

When the toxic component influences the complete cell or just *Km*, the most sensitive setting is at the highest possible overpotential (250 mV) for every concentration χi. When the toxic component only influences *K*1 or *K*2, however, the most sensitive overpotential is lower than 250 mV, that is at 112 and 100 mV. Lower inhibition, thus higher values of $Ki/(Ki + \chi i)$ shift the goal point somewhat downwards. When the toxic component concentration is, for instance, 0.1 mmol/l, the maximum of $dI/d\chi i$ from model IK1 lies at an overpotential of 105 mV. This means that, for $Ki = 1$ mmol/l, the maximum shifts 7 mV to the left as compared to a concentration of toxicity of 2 mmol/l. The optimum of model IK2 shifts from 100 mV at $\chi i = 2$ mmol/l to 76 mV at $\chi i = 0.1$ mmol/l. We would like to detect very low concentrations of toxic components. Even of components that are not very harmful to the bacteria. This implies that choosing a lower overpotential set point ensures a higher sensitivity at low concentrations.

Thus, for model IK1 and IK2, the overpotential related to a maximum sensitivity is a function of the toxicity itself. This phenomenon increases the difficulty to make a good choice for overpotential. The setting of the most sensitive sensor is not only determined by the mode of action of the toxic component, but it also depends on the ratio between *Ki* and χi in the case of models *K*1 and IK2.

3.3. Robustness

In a real application the sensor will be used in an environment that undergoes changes that are not toxic. For example pH, conductivity or transfer rates may change. These changes in the environment should not influence the detection of toxic components too much. In other words, the detection of toxicity should be robust against changes in parameters other than toxicity. Hence the setting of the biosensor should be such that the sensor is sensitive to change in toxic component concentration and at the same time insensitive to changes over time of other components and model parameters. In what follows, it will be investigated how changes in model parameters affect $dI(\eta)/d\chi i$ and what the consequences are for an optimal choice of η. Recall that the model parameters were estimated under non-toxic conditions. When the sensor is applied, these parameters may change over time. Furthermore, the initial parameter estimates may not be very accurate and may influence the choice for an optimal overpotential. It was investigated how the optimal overpotential setting is influenced by the initial estimates of those parameters that were estimated less accurately.

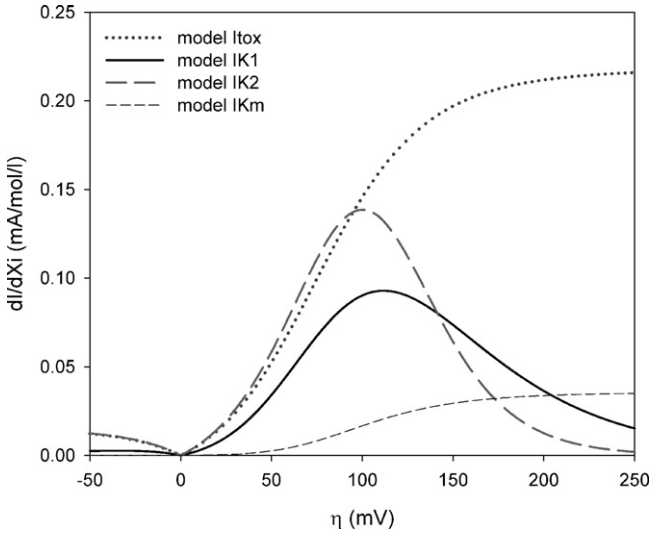

Fig. 3. Sensitivity to a change of toxic component concentration ($\chi i = 2$ mmol/l), as a function of overpotential. When $dI/d\chi i$ is maximal, the sensor is most sensitive to toxic components.

In the models (Eqs. (2)–(5)) the following parameters are present: I_{max}, *K*1, *Km*, α, *K*2, *Ki* and the process variable S, the substrate concentration. I_{max} is determined by the capability of the bacteria under non-toxic conditions. Hence, its initial value can be estimated quite accurately. It is also not likely to change over time. The model parameters α and *Km* can be determined under non-toxic conditions and are not expected to change over time.

*K*1 represents the ratio of the biochemical over the electrochemical reaction rate constants that is $K1 \sim I_{max}/I_{ex}$, where I_{ex} (mA) is the exchange current density under zero-current conditions at equilibrium. This exchange current density will not change unless there are redox active components present that can be regarded toxic. Therefore, under non-toxic conditions, *K*1 will not change. Recall that $K1 = 1$ is chosen on the basis of existing datasets (Hamelers et al., 2011). However, if *K*1 would have a different value, it will possibly affect the sensitivity. Model simulations reveal that in the range $0.1 < K1 < 50$ the optimal overpotential for the model Itox and IKm remains at the highest investigated point, 250 mV. For model IK1 a higher value of *K*1 results in a higher sensitivity at all overpotentials. The optimal value of the overpotential increases. However, a good sensitivity is still found at an overpotential of 112 mV, as found to be optimal for the parameter values of Table 1. Model IK2 on the other hand, gives a lower sensitivity, if *K*1 increases. The optimal overpotential increases just as in model IK1. Choosing a value to control the overpotential is then dependent on the accuracy of estimation of *K*1, the accuracy of the current measurements and the value of current itself.

Model parameter *K*2 represents the forward over the backward biochemical rate constants. This value can change over time especially when water conditions like pH change. Protons are produced as product and pH greatly influences the speed of the forward reaction rate. Therefore, it is important to see if the choice of overpotential for maximum sensitivity of the sensor changes when the value of *K*2 changes. Also, the substrate concentration can change over time. Hence, the robustness of $dI/d\chi i$ for changes in *K*2 and *S* was determined. The biosensor is more robust to changes in the parameter, if the absolute value of the derivative of $dI/d\chi i$ with respect to a specific parameter is as low as possible. Hence, with respect to robustness, the goal is to select η such that

$$\eta^* = arg \min_{\eta \in [-50,250]} \frac{\partial^2 I}{\partial Xi \partial \Theta} \quad \text{with } \Theta \in \{I_{max}, K1, K2, Ki, S\} \tag{7}$$

Table 3
Overview of robustness of sensitivity for changes in the model parameters $K1$, $K2$ and S of the four models. Least robust means that the sensitivity is changed most at the given overpotential η when the parameter changes. The sensitivity changes least upon change of the parameter at the overpotential that is indicated as most robust.

Model		Model parameter that changes		
		$K1$	$K2$	$K3$
Itox	Least robust	η = 250 mV	η = 250 mV	η = 250 mV
	Most robust	η = 0 mV	η = 0 mV	η = 0 mV
IK1	Least robust	η = 111 mV	η = 73 mV	S = 5 mM η = 120 mV S = 0.5 mM η = 115 mV
	Most robust	η = 0 and 250 mV	η = 0 and 250 mV	η = 0 mV
IK2	Least robust	η = 75 mV	η = 39 and 106 mV	η = 94 mV
	Most robust	η = 0 and 250 mV	η = 0, 66 and 250 mV	η = 0 mV
IKm	Least robust	η = 250 mV	η = 250 mV	η = 250 mV
	Most robust	η = 0 mV	η = 0 mV	η = 0 mV

In other words, the change of sensitivity, $dI/d\chi i$, is minimal at a change of parameter Θ at overpotential η^*. The derivative of $dI/d\chi i$ with respect to $K2$ and S is investigated as a measure for robustness. When the toxic component acts on microorganisms according to model Itox and model IKm, the current is most robust for changes in $K2$ and S when the overpotential is equal to 0 mV. However, from Fig. 3, it can be seen that this is also the overpotential at which the current is least sensitive for changes in concentration χi. The current is most sensitive at a high overpotential, but here it is also least robust.

When the toxic component influences the microorganisms according to model IK1 the sensitivity for toxic components is influenced when model parameter $K2$ changes. This influence is the largest for an overpotential of 73 mV and smallest when the overpotential is very low (around 0 mV) or very high (250 mV). Changes in S will influence the detection of toxicity the most at overpotential of 120 mV. However, the concentration of substrate is of great influence on this. For a substrate concentration of 5 mmol/l a change will hardly affect the detection of toxic components. However, when the substrate concentration is 0.5 mmol/l, the biosensor will be less robust and a lower substrate concentration will lower the sensitivity and thus the limit of detection of toxic components.

When the toxic component influences the microorganisms according to model IK2, a similar effect is seen for changes in S as compared to model IK1. The sensor would be least robust at an overpotential of 94 mV and most robust at low (0 mV) and high overpotentials. For changes in $K2$, however, the biosensor is most robust at low and high overpotentials but also at 66 mV. An overview of the presented values is given in Table 3. All data were calculated using the parameter values from Table 1. When a different system is used the parameter values may be different, but these values can easily be obtained under non-toxic conditions. Also, the values for the optimal control of overpotential in view of sensitivity and robustness have to be adjusted, but the four models still give a good indication for the different type of responses that can be expected from toxic contamination.

3.4. Tradeoff between sensitivity and robustness

To control the sensor at an overpotential that gives a sensitive sensor for toxic components, but is also robust for changes in the other parameters, a trade off has to be made. The noise of the current measurement and the absolute value of current should be taken into account when this trade-off is made. In Fig. 4 the sensitivity for toxicity ($dI/d\chi i$) is plotted, as well as the effect of changes in $K2$ on this sensitivity ($(\partial^2 I)/(\partial\chi i\,\partial K2)$) for model IK1 and the concentration χi = 0.1 mmol/l. The solid line shows the sensitivity and has a maximal value at 104 mV. At this overpotential the sensor is most sensitive. The black dotted line shows the effect a change of $K2$ has on the sensitivity. The sensor is most robust when this value is very low, thus at an overpotential of 0 or 250 mV and least robust at an overpotential of 72 mV. When the sensor is controlled at 104 mV, a change in $K2$ will affect the sensitivity. Controlling the sensor at a value between 72 and 104 mV will make the sensor less sensitive and less robust. However, controlling the sensor at a value just above 104 mV e.g. 120 mV, the sensor will be a little less sensitive for toxicity but more robust for $K2$. Hence, a feasible interval for η, such that the sensor has the required minimum sensitivity and maximum robustness ($\partial^2 I)/(\partial\chi i\,\partial K2$), can be chosen graphically. In the area where these two areas overlap, the overpotential should preferably be controlled. In Fig. 4 the sensitivity is set at a minimum of 0.1 mA/mmol/l and thus the overpotential should lie between 75 mV and 140 mV. The maximum of the influence of $K2$ is set at 0.002 mA/mmol/l. Hence, the overpotential should then be controlled at values below 31 mV or above 118 mV. The overlapping dashed area shows that the overpotential should be controlled between 83 and 140.3 mV to obey both requirements.

The effect of the substrate concentration has also been investigated. Keeping substrate concentration high, results in a much more robust sensor for changes in substrate concentration than for low substrate concentration (not shown).

To determine the best setting for the overpotential, this tradeoff can be made for each model, using parameter values and required levels for sensitivity and robustness applicable for the system used.

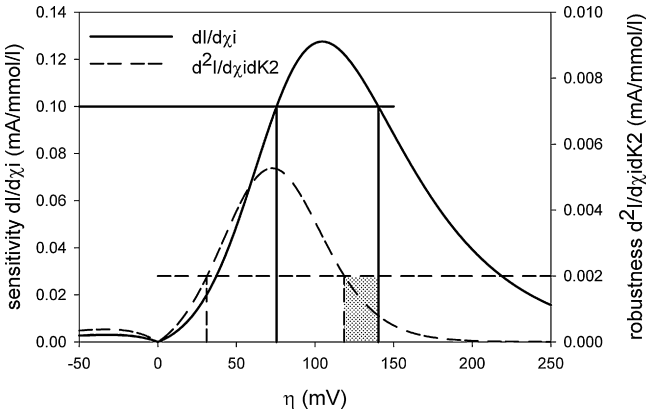

Fig. 4. Model IK1: sensitivity for toxicity ($dI/d\chi i$), χi = 0.1 mmol/l, compared with robustness against changes in parameter $K2$. When the sensitivity is chosen to be at least 0.1 and the influence of $K2$ on the sensitivity to be at the most 0.002, the overpotential has to lie between 118 and 140 mV. (—) primary y-axis $dI/d\chi i$, (- - -) secondary y-axis $d^2I/d\chi i\,dK2$.

4. Discussion

When the type of component that may pass the sensor is unknown, the sensor has to be controlled at an overpotential at which the sensitivity is high for all four models. This means that a trade-off has to be made for the choice of the overpotential. Choosing an overpotential between 76 mV and 104 mV gives a very sensitive sensor for components that influence $K1$ or $K2$. When a component influences Km, however, and the sensor is controlled at 76 mV, the change in current is very low. Controlling the overpotential at 250 mV gives a sensitive sensor for components that influence the complete metabolism or Km, but a very poor sensitivity for components influencing $K1$ and $K2$. The choice of an optimal overpotential is thus very much affected by the kind of contaminations that are expected. If this is not known, an overpotential of e.g. 150 mV gives a relatively good sensitivity for any kind of component, but is not optimal. Another option would be to make the sensor in duplex and control the two sensors at different overpotential, preferably one between 75 and 100 mV and the other one at 250 mV. By comparing the change of the current in the set-ups, something may already be concluded about the mode of action of the component and maybe even about the type of component.

For example, a database with different toxic components and related value for Ki and type of kinetic model can be set-up. Values for the model parameters can also be determined from polarization curves made under non-toxic condition. By making a polarization curve at the moment a change in current is observed, it can be determined what the appropriate model is and what the value of the inhibition term $Ki/(Ki + \chi i)$ is. By combining the database of Ki's and the model, with the value of the inhibition term, the concentration for each possible component can be estimated.

The models presented in this paper are derived under steady state conditions. They do not take the specific design of the sensor into account, only the biofilm. To enable online signal processing of the data from the sensor, the modified Butler–Volmer–Monod model (Eqs. (2)–(5)) must be embedded in a reactor model, in order to account for sensor cell processes such as wash out. When the toxic component enters the sensor, the dynamics of the current change before reaching the new pseudo-steady state can also give information about the type and concentration of component present.

5. Conclusion

The sensitivity of current change in a microbial fuel cell based biosensor depends on several factors, as (i) the mode of action of the component, (ii) the affinity for the toxic component, (iii) the concentration of component and (iv) the overpotential at which the sensor is controlled. This paper shows that the choice of the overpotential at which the sensor is most sensitive depends on the mode of action of the toxic component. The choice of overpotential also depends on the robustness of the sensor against changes in the model parameters. To get a sensitive and robust sensor in the same time, a choice on the basis of the tradeoff between sensitivity and robustness has to be made. This theoretical study provides a basis for the design and performance of experiments that can validate the four models for detection of toxicity using a MFC-based biosensor.

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