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ORIGINAL PAPER

Time averaged concentration calculations in pulse electrochemical machining

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Abstract Simulation of the species concentrations during the Pulse Electrochemical Machining (PECM) process can provide information on system design and guidelines for practical use. In detailed numerical calculations the concentrations will be calculated simultaneously with the temperature due to mutual dependencies. The pulses that are applied to the PECM system have to be described on a time scale that can be orders of magnitude smaller than the physical time scales in the system. If the full detail of the applied pulses has to be taken into account, the time accurate calculation of the variables distributions evolutions in PECM can become a computationally very expensive procedure. In previous work (Smets et al. J Appl Electrochem 37(11):1345, 2007), a time averaging approach was introduced. Performing this, the timesteps used during the calculations are no longer dictated by the pulse characteristics. Using this approach, computationally very cheap, yet satisfying results can be obtained. This work focuses on the behaviour of the concentration evolution. The concentration and the temperature calculation have different requirements for optimal approximated calculations, and a compromise has to be found between them. An analysis is performed on a simplified model, which provides useful guidelines during simulations.

Keywords Pulse electrochemical machining · Concentration distribution · Concentration evolution · Time averaging · Transient

List of symbols

c	Concentration (mol m^{-3})
$\bar{c}$	Averaged concentration (mol m^{-3})
$\tilde{c}$	Concentration ripple (mol m^{-3})
c_{decay}	Concentration decaying component (mol m^{-3})
D	Diffusion coefficient (m^2 s^{-1})
E	Error function (%)
F	Faraday constant (=96,485 C mol^{-1})
J	Current density distribution (A m^{-2})
n	Valence (−)
$\bar{r}$	General location vector (m)
t	Time (s)
t'	Time (s)
T	Pulse period (s)
T'	Dimensionless pulse period (−)
$\bar{v}$	Velocity vector (m s^{-1})
x	Distance (m)
α	Duty cycle (−)
δ	Nernst diffusion layer thickness (m)
λ	Time (s)
τ	Time constant (s)
Φ_c	Mass flux (mol s^{-1} m^{-2})
ψ	Pulse delay (s)
ψ^*	Optimal pulse delay (s)
ψ_{limit}	Limit pulse delay (s)

Abbreviations

1D	One dimensional
ECM	Electrochemical machining
PECM	Pulse electrochemical machining
QSS	Quasi steady state
QSSSC	Quasi steady state shortcut
SS	Steady state

1 Introduction

Electrochemical machining (ECM) is a manufacturing process based on the controlled anodic dissolution of a

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metal at large current densities (in the range of 1 A mm^{-2}). An electrolyte is used to carry away produced heat and mass, among other reaction products.

Despite its advantages, some difficulties still trouble the application of ECM. One important issue is the lack of quantitative simulation software to predict the tool shape and machining parameters necessary to produce a given work-piece profile [1–3]. The most complete model needs to deal with the effects of the fluid flow, gas evolution, heat generation, the electrochemical processes at the electrodes, the transport of the species involved and all this while the electrode shape changes. This work makes a contribution in calculating the species concentrations.

Pulse electrochemical machining (PECM) involves the application of current or voltage pulses. In this work only current pulses will be considered. This does not compromise the generality, since voltage and current are closely related. Pulsed current is applied for reasons of accuracy and surface quality [3–6].

To simulate electrochemical processes with current pulses, one has to perform calculations with boundary conditions that vary in time. By applying a time stepping algorithm, all the variable distributions are calculated in time. The applied pulses have to be described on a time scale that can be orders of magnitude smaller than the time scale on which physical effects in the system evolve. This means that a lot of timesteps would have to be calculated to perform a satisfying simulation, which would be a computationally very expensive procedure.

A solution to this problem is given in [7], where the temperature evolution was calculated. The hybrid calculation was introduced in the work as an economical solution to the problem. It consists of applying averaged boundary conditions first, and applying pulses starting from a time of interest t^*. A special case of the hybrid calculation is the Quasi Steady State ShortCut (QSSSC), where the averaged SS is used as a starting state, and pulses are applied afterwards. Decomposition of the variable was performed, and will be reused in this work. It was shown that delaying the start of the pulse in time with a certain value ψ, influences the accuracy of the approximative method. Analytical formulae for optimal values of ψ were presented in the work. Also a function E was defined to quantify how well the QSS is approximated, by using the QSSSC.

In the current work an analogous path is followed to calculate the species concentrations. The boundary conditions for the mass production will be averaged. The QSSSC will be applicable for calculating the concentration QSS too. When performing a simulation, and calculating the temperature and concentrations simultaneously, a different optimal pulse delay ψ^* will be needed for optimal approximative calculations for each variable. Only one ψ^* can be applied however, and a compromise has to be found to achieve optimal results. This problem will be addressed in this paper.

Secondary reactions of the produced species are not considered.

2 Mathematical model

The concentration distribution evolution $c(\bar{r}, t)$ in the system is calculated using a convection–diffusion equation,

$$\frac{\partial c}{\partial t} + \bar{v} \cdot \overline{\nabla} c = \overline{\nabla} \cdot \left(D \overline{\nabla} c \right). \tag{1}$$

Mass production is considered at the electrode, and is imposed as flux Φ_c at the electrode surfaces contiguous to the electrolyte.

$$\Phi_c = D \frac{\partial c}{\partial x} = \frac{J}{nF}. \tag{2}$$

The efficiency is 100%, i.e. all the current is considered to be consumed for the production of c.

3 Time averaging

The same averaging technique as formerly applied to the temperature evolution [7] will be applied in this context.

A time averaging operator $\langle \cdot \rangle$ was defined as

$$\langle \varphi(t) \rangle = \frac{1}{T} \int_{t-T+\Gamma}^{t+\Gamma} \varphi(\lambda) \mathrm{d}\lambda, \tag{3}$$

where averaging is performed over the region of one period T, and where Γ provides the freedom of placing the integration interval around t in an arbitrary way. Note that the averaged quantity is undefined in the first $T - \Gamma$ and the last Γ of the time interval under consideration, which will be neglected.

The average mass production at the electrode surface can be easily calculated from the mass production during the on-time of the pulses $\Phi_{c,\mathrm{on}}(\bar{r})$, as

$$\langle \Phi_c(\bar{r}, t) \rangle = \alpha \Phi_{c,\mathrm{on}}(\bar{r}). \tag{4}$$

$\langle \Phi_c(\bar{r}, t) \rangle$ is constant in time and will be used over the whole time interval.

4 Averaging the analytical solution of a simple problem

The problem will be described in one spatial dimension (1D). One electrode is considered. The electrode is regarded as surrounded by an adherent layer of electrolyte of uniform thickness through which diffusion takes place [8],

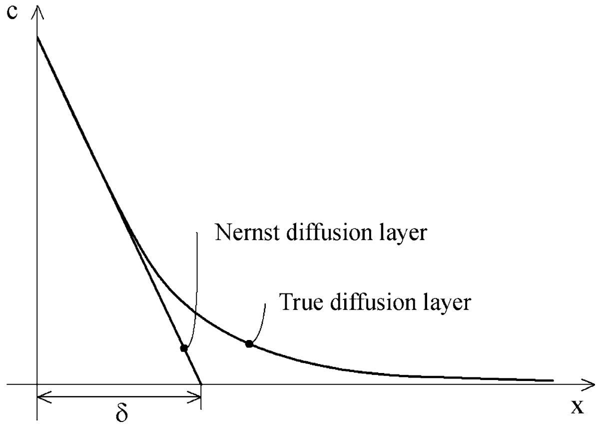

Fig. 1 Nernst diffusion layer, and true diffusion layer. Steady state case

i.e. a Nernst diffusion layer. The Nernst diffusion layer is a linear approximation for the true diffusion layer. The closer to the electrode, the better the approximation, see Fig. 1.

In the Nernst diffusion layer only diffusion is considered, reducing Eq. 1 to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{5}$$

Concentration $c(x, t)$ will be produced at the contact surface between the electrode and the electrolyte, giving rise to the boundary condition

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = \frac{J}{nFD}. \tag{6}$$

The initial condition is that $c = 0$ at $t = 0$. We also have $c = 0$ at $x = \delta$, where δ is the thickness of the Nernst diffusion layer.

The transient concentration is described in literature [8]. After rewriting the equations a bit, one obtains

$$\frac{c(x,t)}{c^*} = \begin{cases} 0, & \text{for } t' \le 0, \\ \sum_{k=1}^{\infty} \beta_k(x)\left[1 - \frac{e^{T/\tau_k} - e^{\alpha T/\tau_k}}{e^{T/\tau_k}-1} e^{-(t'-iT)/\tau_k} \right. & \\ \qquad \left. - \frac{e^{\alpha T/\tau_k}-1}{e^{T/\tau_k}-1} e^{-t'/\tau_k}\right], & \text{on-time,} \\ \sum_{k=1}^{\infty} \beta_k(x)\left[\frac{e^{-\alpha T/\tau_k}-1}{e^{-T/\tau_k}-1} e^{-(t'-iT-\alpha T)/\tau_k} \right. & \\ \qquad \left. - \frac{e^{\alpha T/\tau_k}-1}{e^{T/\tau_k}-1} e^{-t'/\tau_k}\right], & \text{off-time,} \end{cases} \tag{7}$$

with

$$\beta_k(x) = \frac{8}{\pi^2(2k-1)^2}\cos\left(\frac{(2k-1)\pi}{2}\frac{x}{\delta}\right), \tag{8}$$

$$\tau_k = \frac{4\delta^2}{\pi^2 D(2k-1)^2}, \tag{9}$$

and

$$c^* = \frac{J_{\text{on}}\delta}{nFD}. \tag{10}$$

To provide a degree of freedom which will be exploited later, the time t', which lags ψ to t, is introduced

$$t' = t - \psi. \tag{11}$$

Note that

$$\sum_{k=1}^{\infty} \beta_k(x) = 1 - \frac{x}{\delta}. \tag{12}$$

These equations are similar to the equations for the temperature evolution in the electrode [7]. The only difference is the definition of the coefficients $\beta_k(x)$ and τ_k, which can easily be seen in the form the equations are in. Because of the similarity of equations, many of the conclusions from [7] can be transferred to this work.

This means that the concentration can be decomposed as [7]

$$c(x,t) = \bar{c}(x,t) + \tilde{c}(x,t) + c_{\text{decay}}(x,t), \tag{13}$$

where $\bar{c}(x,t)$ is the averaged concentration, $\tilde{c}(x,t)$ is the ripple (with an average of zero), and $c_{\text{decay}}(x,t)$ is a decaying component. The averaged concentration $\bar{c}(x,t)$ can be obtained by applying the averaged mass flux (see Eq. 4) to the system [7], which yields

$$\bar{c}(x,t) = \sum_{k=1}^{\infty} \beta_k(x)\left[c^*_{\text{av}}\left(1 - e^{-t/\tau_k}\right)\right], \tag{14}$$

where $c^*_{av} = \alpha c^*$. The ripple $\tilde{c}(x,t)$ can be obtained by diminishing the QSS with its averaged value, which yields

$$\frac{\tilde{c}(x,t)}{c^*} = \begin{cases} \sum_{k=1}^{\infty} \beta_k(x)\left[1 - \frac{e^{T/\tau_k} - e^{\alpha T/\tau_k}}{e^{T/\tau_k}-1} e^{-(t'-iT)/\tau_k} - \alpha\right], & \text{on-time,} \\ \sum_{k=1}^{\infty} \beta_k(x)\left[\frac{e^{-\alpha T/\tau_k}-1}{e^{-T/\tau_k}-1} e^{-(t'-iT-\alpha T)/\tau_k} - \alpha\right], & \text{off-time,} \end{cases} \tag{15}$$

The expression for the decaying component $c_{\text{decay}}(x, t)$ is

$$\frac{c_{\text{decay}}(x,t)}{c^*} = \sum_{k=1}^{\infty} \beta_k(x)\left(\alpha - \frac{e^{\alpha T/\tau_k}-1}{e^{T/\tau_k}-1} e^{\psi/\tau_k}\right) e^{-t/\tau_k}. \tag{16}$$

By varying the parameter ψ, $c_{\text{decay}}(x, t)$ can be influenced. The aim is to make $c_{\text{decay}}(x, t)$ preferably zero or by default as small as possible as quickly as possible. Expression 16 cannot be made exactly zero by the choice of the one degree of freedom ψ. To obtain a closed form expression, no optimisation algorithm is applied, but instead the component for which $k = 1$ will be made zero. This component is the largest in amplitude, and the slowest to damp out. The following optimal value for ψ is obtained,

$$\psi^* = \tau_1 \ln\left(\alpha \frac{e^{T/\tau_1} - 1}{e^{\alpha T/\tau_1} - 1}\right). \tag{17}$$

By making $c_{\mathrm{decay}}(x, t)$ as small as possible as quickly as possible, Eq. 13 simplifies to

$$c(x,t) \approx \bar{c}(x,t) + \tilde{c}(x,t). \tag{18}$$

It is possible to combine the averaged boundary conditions and pulses in one calculation. These calculations were called hybrid [7]. Starting from $t = 0$, the averaged mass sources are applied, and after time $t = t^*$, pulses are applied (possibly delayed by ψ). It can be shown that the concentration is composed of the averaged component $\bar{c}(x,t)$, and the ripple $\tilde{c}(x,t-t^*)$ and a decaying component $c_{\mathrm{decay}}(x,t-t^*)$ starting from the time $t = t^*$:

$$c_{\mathrm{hybrid}}(x,t) = \bar{c}(x,t) + \tilde{c}(x,t-t^*) + c_{\mathrm{decay}}(x,t-t^*). \tag{19}$$

A particularly interesting case, is when $t^* \to \infty$ s. The starting state at $t = t^*$ is then the averaged SS. This situation is called the QSSSC [7]. When performing the QSSSC, it is convenient to start the pulsed calculation from $t^* = 0$ s, while applying the averaged SS as initial state. Note that in this case, the averaged concentration reduces to $\bar{c}(x,t) = c^*_{\mathrm{av}}(1 - \frac{x}{\delta})$:

$$c_{\mathrm{QSSSC}}(x,t) = c^*_{\mathrm{av}}\left(1 - \frac{x}{\delta}\right) + \tilde{c}(x,t) + c_{\mathrm{decay}}(x,t). \tag{20}$$

The transient concentration evolution, together with the QSSSC, is calculated for a case where $\alpha = 0.5$ and $T' = 0.25$, where

$$T' = \frac{TD}{\delta^2}. \tag{21}$$

By not delaying the pulses in time, the results from Fig. 2 are obtained. By delaying the pulses with ψ^*, the results from Fig. 3 are obtained. It can be seen that by delaying the pulses with ψ^*, $c_{\mathrm{decay}}(x, t)$ can be reduced significantly.

Since the full transient calculation and the QSSSC contain exactly the same $c_{\mathrm{decay}}(x, t)$, only the QSSSC will be studied from here. The more accurate the QSSSC approximates the real QSS, the better. The difference between the QSSSC and the QSS, will be quantified with the error function E (in %) [7], which is defined as

$$E_j = \frac{\int_{\delta_j} |c_{\mathrm{QSSSC}}(x,t) - c_{\mathrm{QSS}}(x,t)|\mathrm{d}t}{\int_{\delta_j} c_{\mathrm{QSS}}(x,t)\mathrm{d}t} 100 = \frac{\int_{\delta_j} |c_{\mathrm{decay}}(x,t)|\mathrm{d}t}{\int_{\delta_j} c_{\mathrm{QSS}}(x,t)\mathrm{d}t} 100, \tag{22}$$

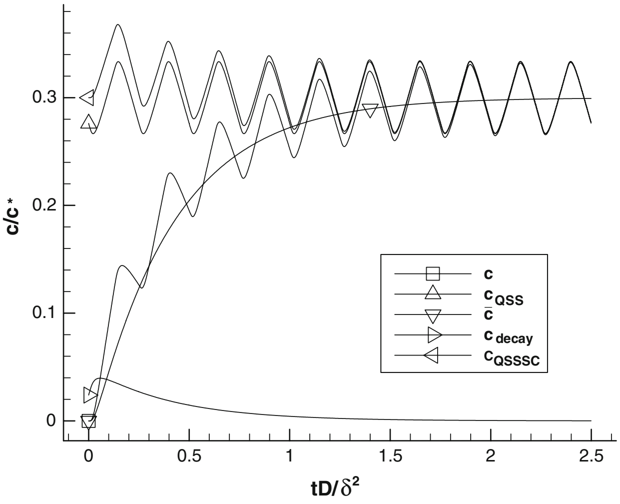

Fig. 2 Concentration evolution, $\psi = 0$ ($\alpha = 0.5$, $T' = 0.25$, $x/\delta = 0.4$)

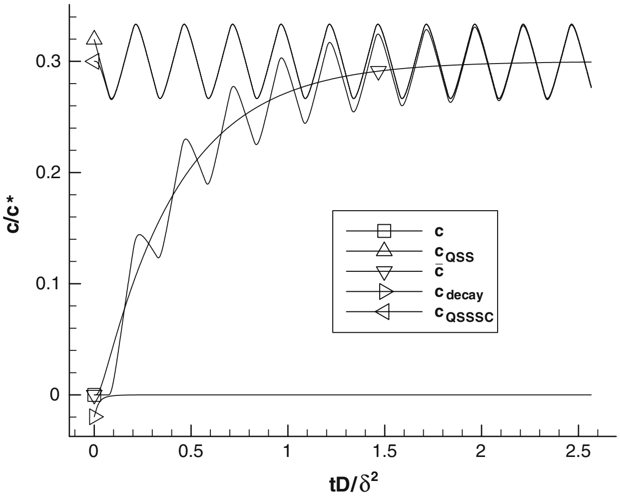

Fig. 3 Concentration evolution, $\psi = \psi^*$ ($\alpha = 0.5$, $T' = 0.25$, $x/\delta = 0.4$)

where the integrals are calculated over δ_j, which is the jth on-time. The integration domain is limited to the on-times, because this is the only interval of interest while performing calculations for PECM. During the on-time of the pulse the actual shape change of the workpiece occurs, which is the ultimate goal for simulations on PECM. The states during the off-times are of no primary importance.

For x/δ from about 0.6 to 1, the solution in Eq. 7 gives a permanent underestimation for the real $c(x, t)$. This can also be seen in Fig. 1 for the SS case. It has to be noted that the impact of this underestimation is limited on the accuracy of E. Apart from the underestimation the shape of $c(x, t)$ is fairly accurate, and because the ratio is taken between two

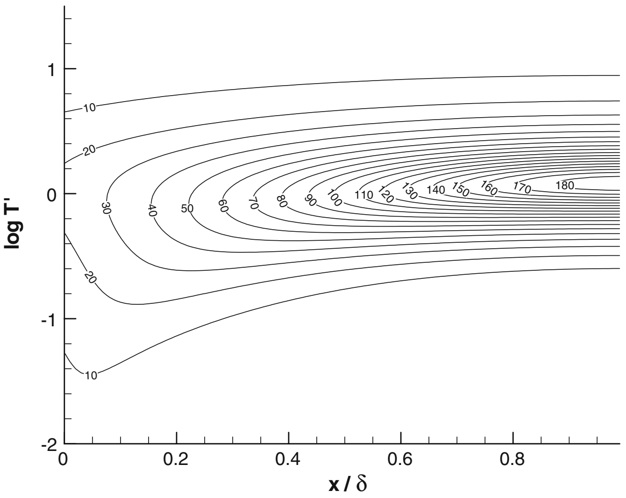

Fig. 4 E_1 as a function of T' and x/δ, for $\alpha = 0.1$. $\psi = 0$

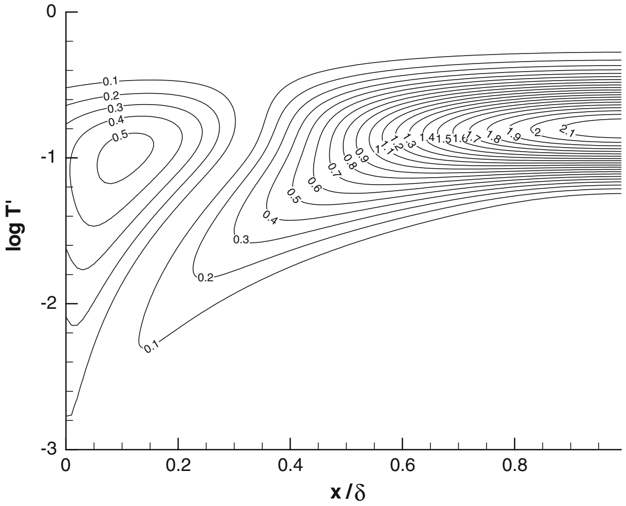

Fig. 5 E_1 as a function of T' and x/δ, for $\alpha = 0.1$. $\psi = \psi^*$

underestimated values, the underestimation is largely canceled out. For x/δ greater than 1, no other results than the approximation $c(x > \delta,\ t) = 0$ are available with this method, and hence no conclusions on E can be made.

E_j is mainly function of three dimensionless parameters: $T' = \frac{\alpha' T}{H^2}$, α and x/δ. Two additional parameters are the number of on-time j, and ψ. E_1 is shown in Fig. 4 for $\alpha = 0.1$, with $\psi = 0$, and in Fig. 5 for the same setup, but with $\psi = \psi^*$.

For the dependancy of E on α, one can generally say: the smaller α, the higher is E.

The following general conclusions can be drawn from the analysis of the E function. If α is limited to the interval [0.1, 1] and x/δ to [0, 0.99], the worst case values of E can be found in Table 1. It can be seen that the worst case E_1 encountered with $\psi = 0$ is about 187%, which is unacceptable. Calculating until the second on-time during the QSSSC, we could still encounter a maximum E_2 of 25.1%. By delaying the pulses with $\psi = \psi^*$, the worst case values of E are drastically reduced. It can be seen from Table 1, that the maximum error E_1 is about 2.19%, which is very acceptable. Calculating until the second on-time gives us a maximum E_2 of about 0.32%. Note that this is a worst case scenario, so most cases perform even better than the values from Table 1.

Table 1 Worst case values of E, (minimal value of α: 0.1)

ψ	E_1 max. (%)	E_2 max. (%)
0	187	25.1
ψ_{limit}	20.4	2.15
ψ^*	2.19	0.32

For the temperature evolution in the system also an optimal ψ^* exits, to minimize the decaying component on the temperature evolution [7]. The pulse delay for the concentration and the temperature have to be taken the same, since they result from the same current pulses. Because the time constants of the temperature evolution are generally much larger than those of the concentration evolution, the temperature gets priority in choosing the pulse delay ψ. The cases where the present averaging technique is very important are the cases where the slowest time constant of the temperature evolution is much larger than the pulse period T. For this case the expression for ψ^* simplifies to

$$\lim_{\frac{T}{\tau_1}\to 0} \psi^* \approx \frac{(1-\alpha)T}{2} = \psi_{\text{limit}}. \tag{23}$$

Another limit case is

$$\lim_{\frac{T}{\tau_1}\to \infty} \psi^* \approx (1-\alpha)T. \tag{24}$$

The evolution of ψ^* between the limit cases is shown in Fig. 6 (for $\alpha = 0.1$). In the temperature case we are at the left of the curve. The concentration case will generally be more to the right on the T/τ_1 axis. It can be seen on Fig. 6 that when ψ^* for the concentration deviates most from ψ_{limit}, the point is more to the right on the T/τ_1 axis, i.e. $T \gg \tau$,which makes that the concentration does not accumulate over multiple pulses and hence pulse shifting has become of no importance. Because of this, the error E stays limited for the concentration calculations when ψ_{limit} is applied, as can be seen in Fig. 7 for E_1. The case where $\psi = \psi_{\text{limit}}$ is also noted in Table 1. It can be seen that however the pulse delay is not optimally chosen, the decaying component is still acceptably low, if the calculation is continued until the second on-time.

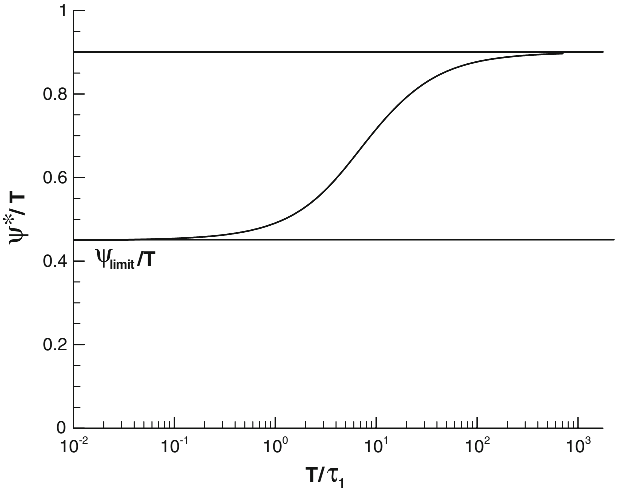

Fig. 6 $\frac{\psi^*}{T}$ as a function of $\frac{T}{\tau_1}$, (for $\alpha = 0.1$)

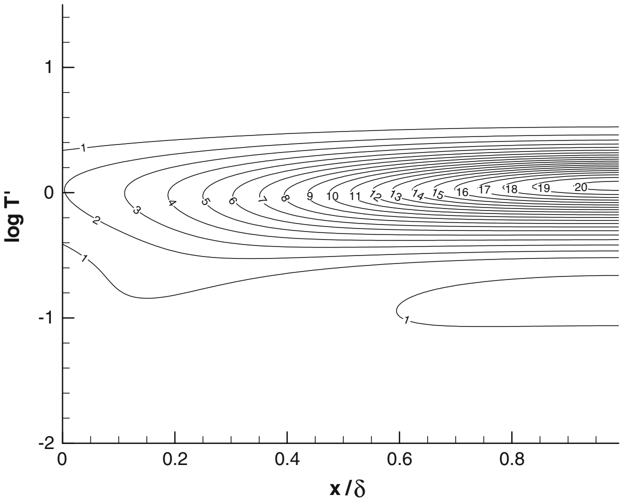

Fig. 7 E_1 as a function of T', for $\alpha = 0.1$. $\psi = \psi_{\text{limit}}$

5 Conclusions

The applied averaging technique adopted in earlier work for the calculation of temperature transients in electrochemical systems during PECM is adopted for the calculation of concentration transients. For concentration calculation this averaging technique is generally not of vital importance, because the transient is usually not very long. The idea is to combine both the temperature and concentration calculations in one step, and hence the averaging technique is also applied to the concentration evolution.

The averaging technique applies very well to the concentration evolution, but the problem arises that the calculation of the temperature and concentrations require different optimal pulse shifts ψ^*. As generally the slowest time constant τ_1 of the temperature evolution is longer than the slowest time constant τ_1 of the concentration evolution, priority is given to the temperature calculation. This proves to be a good compromise for the theoretical case treated in this paper. When the slowest time constant τ_1 of the temperature evolution is much larger than the pulse period T, the compromise made in the choice of $\psi = \psi_{\text{limit}}$ performs well under all circumstances. Already during the second on-time in the QSSSC, the calculated variables are acceptable.

The assumptions of the models used to derive the analytical solutions are too strict for real life Electrochemical Machining (ECM) conditions. Nevertheless, very interesting conclusions are made which will be used in future work. The results also apply very well as practical rules of thumb when using the hybrid technique during complex numerical calculations.

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