Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Kinetics of the electrochemically-assisted deposition of sol-gel films

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Supporting Information

Description of the numerical simulation

By dividing the concerned length and time into small segments Δx and Δt, respectively, the film deposition process can be expressed in numerical form. At $x = 0$, the concentration of OH^- ions is affected by the flux of electrochemical generation and the diffusion:

$$C_{OH^-}(0,t+\Delta t) = C_{OH^-}(0,t) + \frac{\Delta t}{\Delta x^2} D_{OH^-}^{sol}\left(C_{OH^-}(\Delta x,t) - C_{OH^-}(0,t)\right) + \frac{I_F \Delta x}{nFAD_{OH^-}^{sol}} \quad (\text{for } t < t^F) \qquad (Eq.\ 1)$$

$$C_{OH^-}(0,t+\Delta t) = C_{OH^-}(0,t) + \frac{\Delta t}{\Delta x^2} D_{OH^-}^{film}\left(C_{OH^-}(\Delta x,t) - C_{OH^-}(0,t)\right) + \frac{I_F \Delta x}{nFAD_{OH^-}^{sol}} \quad (\text{for } t \geq t^F) \qquad (Eq.\ 2)$$

where $D_{OH^-}^{sol}$ and $D_{OH^-}^{film}$ represent the diffusion coefficients of OH^- ions in the solution and the film, respectively. For $0 < x < l$, the diffusion coefficients of OH^- and $-SiOH$ in the film are concerned.

$$C_{OH^-}(x,t+\Delta t) = C_{OH^-}(x,t) + \frac{\Delta t}{\Delta x^2} D_{OH^-}^{film}\left(C_{OH^-}(x+\Delta x,t) - 2C_{OH^-}(x,t) + C_{OH^-}(x-\Delta x,t)\right) \qquad (Eq.\ 3)$$

$$C_{-SiOH}(x,t+\Delta t) = C_{-SiOH}(x,t) + \frac{\Delta t}{\Delta x^2} D_{-SiOH}^{film}\left(C_{-SiOH}(x+\Delta x,t) - 2C_{-SiOH}(x,t) + C_{-SiOH}(x-\Delta x,t)\right) - \Delta t k_f^{'} C_{OH^-}(x,t)\, C_{-SiOH}(x,t)^2 \qquad (Eq.\ 4)$$

D_{-SiOH}^{film} is the diffusion coefficient of –SiOH in the deposited film. For $x = l$, one has to consider the diffusion flux both in the film and in the solution:

$$C_{OH^-}(x,t+\Delta t) = C_{OH^-}(x,t) + \frac{\Delta t}{\Delta x^2} D^{film}_{OH^-}\left(C_{OH^-}(x-\Delta x,t) - C_{OH^-}(x,t)\right) + \frac{\Delta t}{\Delta x^2} D^{sol}_{OH^-}\left(C_{OH^-}(x+\Delta x,t) - C_{OH^-}(x,t)\right)$$

(*Eq*. 5)

$$C_{-SiOH}(x,t+\Delta t) = C_{-SiOH}(x,t) + \frac{\Delta t}{\Delta x^2} D^{film}_{-SiOH}\left(C_{-SiOH}(x-\Delta x,t) - C_{-SiOH}(x,t)\right) + \frac{\Delta t}{\Delta x^2} D^{sol}_{-SiOH}\left(C_{-SiOH}(x+\Delta x,t) - C_{-SiO}\right. - \Delta t k_f^{'} C_{OH^-}(x,t) C_{-SiOH}(x,t)^2$$

(*Eq*. 6)

D^{sol}_{-SiOH} is the diffusion coefficient of –SiOH in the solution. For $x > l$, the diffusion coefficients in the solution are considered:

$$C_{OH^-}(x,t+\Delta t) = C_{OH^-}(x,t) + \frac{\Delta t}{\Delta x^2} D^{sol}_{OH^-}\left(C_{OH^-}(x+\Delta x,t) - 2C_{OH^-}(x,t) + C_{OH^-}(x-\Delta x,t)\right)$$

(*Eq*. 7)

$$C_{-SiOH}(x,t+\Delta t) = C_{-SiOH}(x,t) + \frac{\Delta t}{\Delta x^2} D^{sol}_{-SiOH}\left(C_{-SiOH}(x+\Delta x,t) - 2C_{-SiOH}(x,t) + C_{-SiOH}(x-\Delta x,t)\right) - \Delta t k_f^{'} C_{OH^-}(x,t) C_{-SiOH}(x,t)^2$$

(*Eq*. 8)

The initial and semi-infinite boundary conditions still apply:

$$C_{OH^-}(x,0) = C^*_{OH^-}$$

(*Eq*. 9)

$$C_{OH^-}(\infty,t) = C^*_{OH^-}$$

(*Eq*. 10)

$$C_{-SiOH}(x,0) = C^*_{-SiOH}$$

(*Eq*. 11)

$$C_{-SiOH}(\infty,t) = C^*_{-SiOH}$$

(*Eq*. 12)

The equations above constitute the basis for the numerical simulation, which was programmed by Fortran 95. The source code and the compiled program are attached. They are also available upon request to the authors.

Nomenclature

Symbol	**SI unit**	**Physical meaning**

x, Δx	m	length in the axis of film thickness, unit length in simulation
t, Δt	s	time, unit time in simulation

(Other symbols can be found in the main text of the publication.)