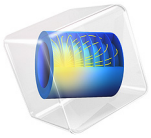


Model created in COMSOL Multiphysics 6.4

Adsorption–Desorption Voltammetry

Introduction

For an electrochemical reaction to occur, the reacting species usually needs to adsorb to the electrode surface before undergoing reduction or oxidation, after which the resulting product species desorbs back into the electrolyte.

If the rate of adsorption or desorption is slow in comparison to the electrochemical charge transfer step, the adsorption–desorption phenomena may have to be accounted for in a model.

This example investigates the impact of various kinetic parameters for adsorption, desorption and electron transfer when performing cyclic voltammetry on a planar disk electrode.

The examples replicates the results of Ref. 1.

Model Definition

The model defines diffusion (by Fick's law) of an electrolyte species in a 1D geometry between $x = 0$ and $x = L$, and the local mass balances of two surface species at an electrode surface located at $x = 0$.

At the electrode boundary ($x = 0$) the electrolyte species A may adsorb according to

$$\mathrm{A} \leftrightarrow \mathrm{A_{ads}}$$

The adsorbed species $\mathrm{A_{ads}}$ may then undergo reduction to form $\mathrm{B_{ads}}$ in a charge transfer reaction according to

$$\mathrm{A_{ads}} + e^- \leftrightarrow \mathrm{B_{ads}}$$

Langmuir isotherms are used for describing the kinetics, with the adsorption rate defined as

$$r_{\mathrm{ads}} = k_{a1} c_{\mathrm{A}} (1 - \Theta_{\mathrm{A_{ads}}} - \Theta_{\mathrm{B_{ads}}}) - k_{d1} \Theta_{\mathrm{A_{ads}}}$$

where k_{a1} is the adsorption rate constant, c_A the electrolyte concentration of species A, $\Theta_{\mathrm{A_{ads}}}$ the electrode surface coverage of species $\mathrm{A_{ads}}$, $\Theta_{\mathrm{B_{ads}}}$ the electrode surface coverage of species $\mathrm{B_{ads}}$, and k_{d1} the desorption rate constant.

The charge transfer reaction is defined as

$$i_{\mathrm{loc}} = k_0 \Gamma F \left(\Theta_{\mathrm{B_{ads}}} e^{\frac{0{,}5\eta F}{RT}} - \Theta_{\mathrm{A_{ads}}} e^{-\frac{0{,}5\eta F}{RT}} \right)$$

where k_0 is the charge transfer rate constant, Γ the density of surface sites at the electrode, F Faraday's constant, R the molar gas constant, T the temperature, and η the overpotential.

The overpotential η is defined as

$$\eta = E - E_0$$

where E is the electrode potential and E_0 the formal potential.

The model is solved in a time-dependent simulation, ramping the potential from +0.5 V to –0.5 V and back, simulating a cyclic voltammogram.

When evaluating the voltammograms below, the total electrode current is defined as

$$I_{\mathrm{tot}} = \pi r_d^2 i_{\mathrm{loc}}$$

where r_d is the radius of the disk electrode.

The initial surface coverage of $\mathrm{A_{ads}}$ is set to $\Theta_{\mathrm{A_{ads}}} = 0$, defining a situation where the cyclic voltammogram is recorded shortly after immersing the electrode in the electrolyte.

Two dimensionless parameters, K' and k_0', are altered in a parametric sweep. They are defined as

$$K' = \frac{k_{a1}}{k_{d1} c_A}$$

and

$$k_0' = \frac{k_0 r_d^2}{D_A}$$

respectively. A high K' value hence represents a fast adsorption/slow desorption case, whereas a high k_0' value represents a case featuring fast charge transfer. The simulated cases are described in Table 1.

TABLE 1: SIMULATION CASES IN THE PARAMETRIC SWEEP.

	K'	k_0'	
Case 1	10^5	10^2	Fast adsorption, fast charge transfer
Case 2	10^{-5}	10^2	Slow adsorption, fast charge transfer
Case 3	10^5	10^{-2}	Fast adsorption, slow charge transfer

Results and Discussion

Figure 1 shows the voltammograms for the three simulated cases. Case 1, with fast adsorption and fast kinetics results in a voltammogram fairly symmetric and centered around $E = 0$ V. The total integral of the reduction current (negative peak) is significantly lower than the integrated oxidation current (positive peak). This is a result of the adsorption–desorption reaction not being in equilibrium ($\Theta_{A_{ads}} = 0$) when the simulation is started.

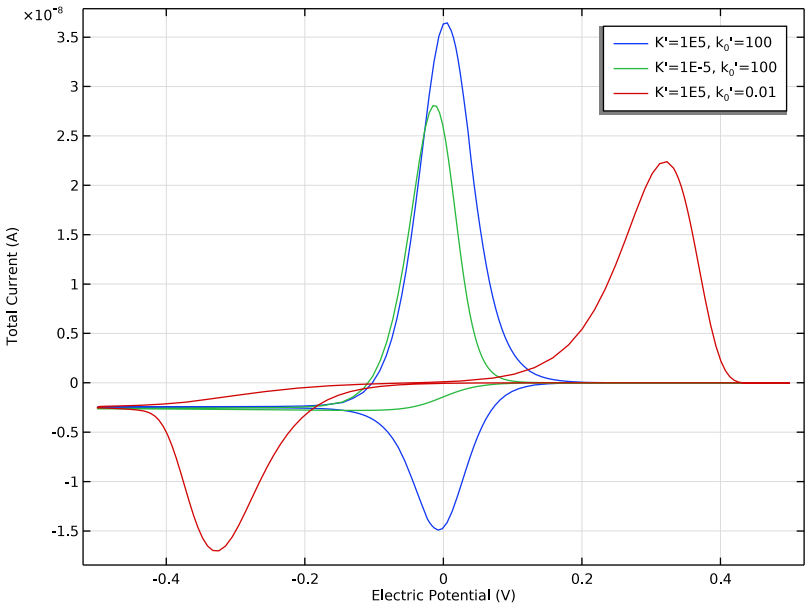


Figure 1: Cyclic voltammograms for the three investigated cases of 1) fast adsorption and charge transfer (blue), 2) slow adsorption and fast charge transfer (green), and 3) fast adsorption and slow charge transfer (red).

Case 2, with slower adsorption, features a limiting reduction current at $E < -0.1$ V, whereas the oxidation peak is fairly similar to that of Case 1.

Case 3, with slower charge transfer kinetics, features a more pronounced separation between the peaks.

More insights may be gained by inspecting the electrode surface coverages of A_{ads} and B_{ads} and the electrolyte concentration of species A at the electrode surface, as is shown in Figure 2 to Figure 4.

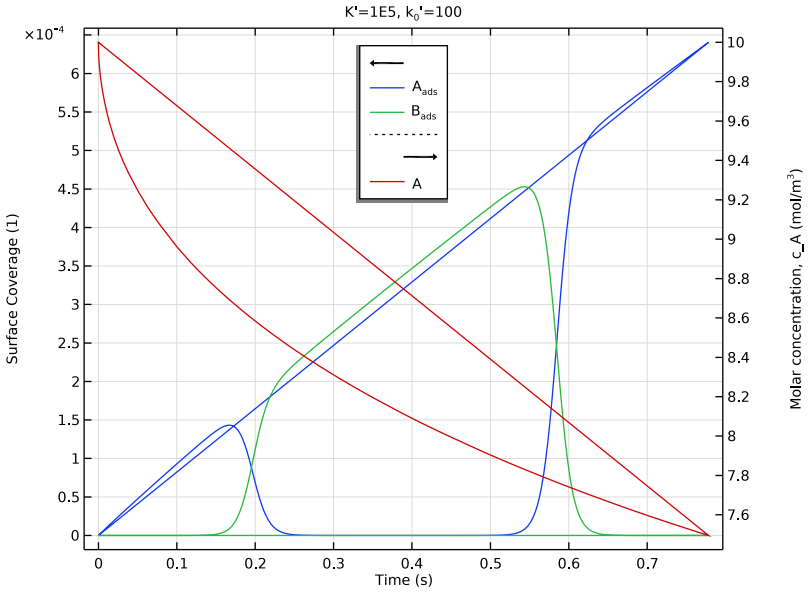


Figure 2: Surface coverages of species A_{ads} and B_{ads} and the concentration of A at the electrode surface for case 1) fast adsorption and fast charge transfer.

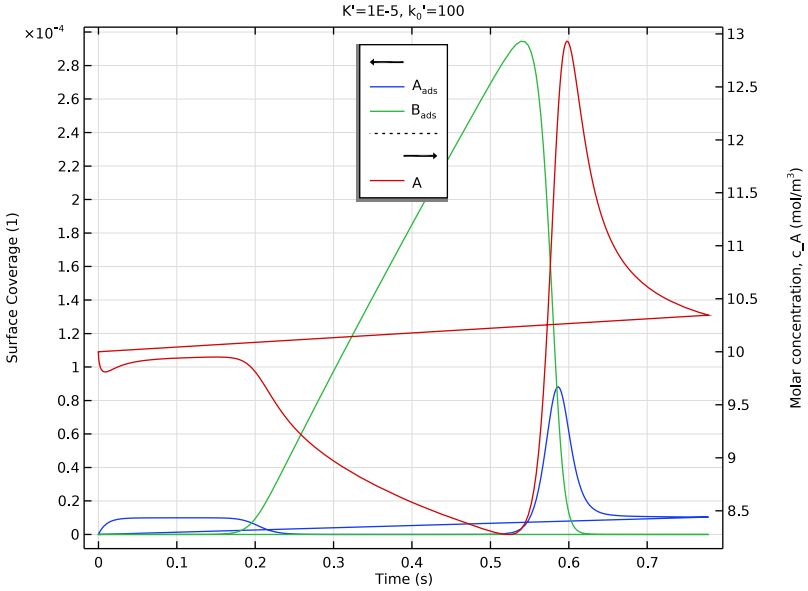


Figure 3: Surface coverages of species A_{ads} and B_{ads} and the concentration of A at the electrode surface for case 2) slow adsorption and fast charge transfer.

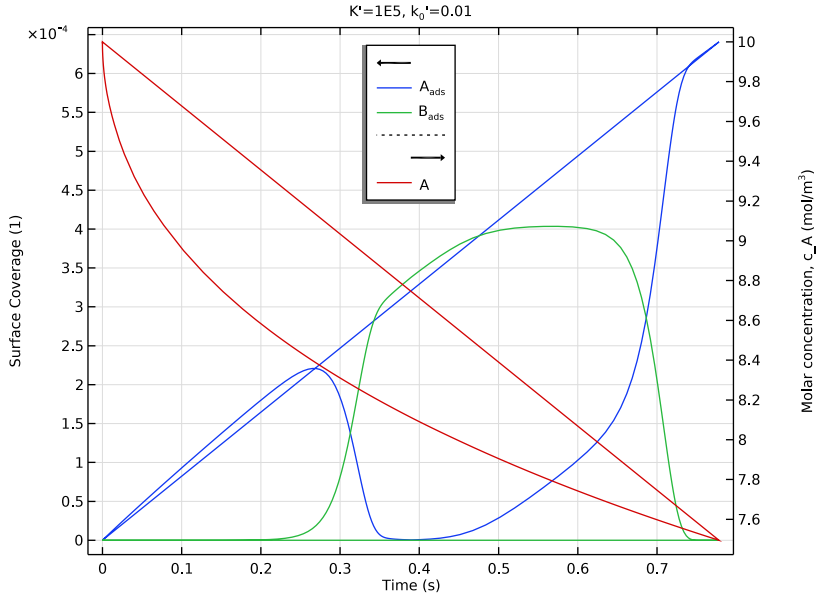


Figure 4: Surface coverages of species A_{ads} and B_{ads} and the concentration of A at the electrode surface for case 3) fast adsorption and slow charge transfer.

Reference

1. F. Chevallier, O. Klymenko, L. Jiang, T. Jones, and R. Compton, "Mathematical modelling and numerical simulation of adsorption processes at microdisk electrodes" *J. Electroanal. Chem.*, vol. 574, pp. 217–237, 2005.

Application Library path: `Electrochemistry_Module/Electroanalysis/adsorption_desorption_voltammetry`

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click — **1D**.

2 In the **Select Physics** tree, select **Electrochemistry** > **Electroanalysis (tcd)**.

3 Click **Add**.

This model will model the transport of one species only (species A) in the electrolyte.

4 In the **Number of species** text field, type 1.

5 In the **Concentrations (mol/m³)** table, enter the following settings:

c_A

6 Click **Study**.

7 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces** > **Cyclic Voltammetry**.

8 Click **Done**.

GLOBAL DEFINITIONS

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `adsorption_desorption_voltammetry_parameters.txt`.

GEOMETRY 1

Interval 1 (i1)

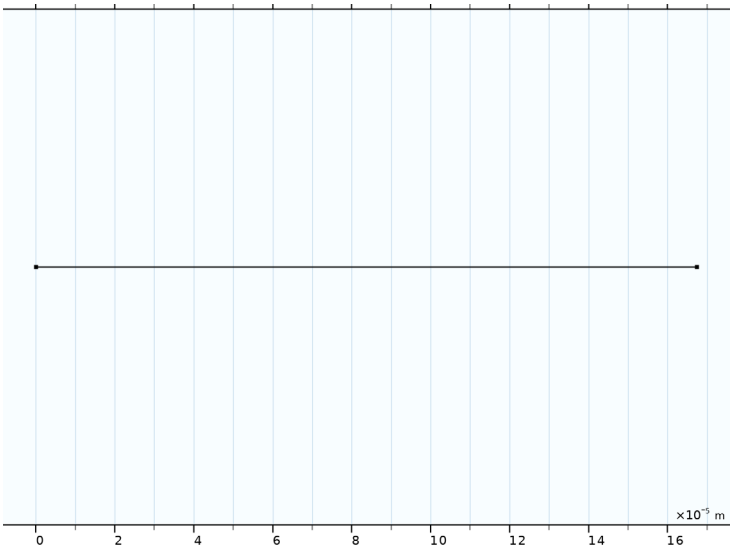
1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

2 In the **Settings** window for **Interval**, locate the **Interval** section.

3 In the table, enter the following settings:

Coordinates (m)
0
L

4 Click **Build All Objects**.



ELECTROANALYSIS (TCD)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Electroanalysis (tcd)**.

2 In the **Settings** window for **Electroanalysis**, locate the **Cross-Sectional Area** section.

3 In the A_c text field, type `A_electrode`.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Electroanalysis (tcd)** click **Electrolyte 1**.

2 In the **Settings** window for **Electrolyte**, locate the **Diffusion** section.

3 In the D_{cA} text field, type `D_A`.

Initial Values 1

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the c_A text field, type `c_A_bulk`.

Electrode Surface 1

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.

You will only work with one electrode surface. Select the boundary to work with by clicking on it in the graphics window on the right:

2 Select Boundary 1 only.

3 In the **Settings** window for **Electrode Surface**, click to expand the **Adsorbing–Desorbing Species** section.

4 In the Γ_s text field, type `Gamma`.

At the electrode surface, we will model the surface coverages of two species (species A_ads and B_ads).

5 Click + **Add**.

6 In the table, enter the following settings:

Species	Site occupancy number (1)
A_ads	1

7 Click + **Add**.

8 In the table, enter the following settings:

Species	Site occupancy number (1)
B_ads	1

9 Locate the **Electrode Phase Potential Condition** section. From the **Electrode phase potential condition** list, choose **Cyclic voltammetry**.

10 In the **Linear sweep rate** text field, type `nu`.

11 In the **Vertex potential 1** text field, type `E_start`.

12 In the **Vertex potential 2** text field, type `E_vertex`.

Electrode Reaction 1

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Model Input** section.

3 From the T list, choose **User defined**. In the associated text field, type `T`.

In the one-electron electrode charge transfer reaction, A_ads gets reduced to form B_ads. The electrolyte species A does not participate in the reaction.

4 Locate the **Stoichiometric Coefficients** section. In the **Stoichiometric coefficients for adsorbing–desorbing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
A_ads	-1
B_ads	1

5 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `E_0`.

6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Concentration dependent kinetics**.

7 In the i_0 text field, type `k0*F_const*Gamma`.

8 In the C_R text field, type `tcd.theta_es1_B_ads`.

9 In the C_O text field, type `tcd.theta_es1_A_ads`.

`tcd.theta_es1_A_ads` and `tcd.theta_es1_B_ads` are the variable names for the surface coverage of A_ads and B_ads, respectively.

DEFINITIONS

Now the adsorption-desorption rate and the reaction, involving species A, A_ads and the amount of free sites, will be defined.

Variables 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.

Define a variable expression for the adsorption rate as follows:

2 In the **Settings** window for **Variables**, locate the **Variables** section.

3 In the table, enter the following settings:

Name	Expression	Unit	Description
`r_ads`	`ka1*tcd.thetafree_es1*c_A-kd1*tcd.theta_es1_A_ads`	mol/(m²·s)	`Adsorption rate`

In the expression above, `tcd.thetafree_es1` is the surface fraction of free sites and `c_A` is the electrolyte concentration of species A. The values of the rate constants `ka1` and `kd1` are specified in the **Parameters** node by the text file you imported earlier.

ELECTROANALYSIS (TCD)

Electrode Surface 1

In the **Model Builder** window, under **Component 1 (comp1)** > **Electroanalysis (tcd)** click **Electrode Surface 1**.

Nonfaradaic Reactions 1

1 In the **Physics** toolbar, click **Attributes** and choose **Nonfaradaic Reactions**.

2 In the **Settings** window for **Nonfaradaic Reactions**, locate the **Reaction Rate** section.

3 Select the **Species c_A** checkbox.

4 In the $R_{0,cA}$ text field, type `-r_ads`.

5 In the **Reaction rate for adsorbing–desorbing species** table, enter the following settings:

Species	Reaction rate (mol/(m^2*s))
A_ads	r_ads

Electrode Surface 1

In the **Model Builder** window, click **Electrode Surface 1**.

Initial Values for Adsorbing–Desorbing Species 1

1 In the **Physics** toolbar, click **Attributes** and choose **Initial Values for Adsorbing–Desorbing Species**.

2 In the **Settings** window for **Initial Values for Adsorbing–Desorbing Species**, locate the **Initial Values for Adsorbing–Desorbing Species** section.

3 In the table, enter the following settings:

Species	Surface coverage (1)
A_ads	theta_A_init

The value of `theta_A_init` is 0, but may changed later in **Parameters**.

MESH 1

To edit the mesh and get a very finely resolved mesh close to the electrode surface, proceed with these steps:

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Edit Physics-Induced Sequence**.

Size

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Mesh 1** click **Size**.

2 In the **Settings** window for **Size**, locate the **Element Size** section.

3 Click the **Custom** button.

4 Locate the **Element Size Parameters** section. In the **Maximum element size** text field, type `L/10`.

5 In the **Maximum element growth rate** text field, type `1.1`.

Size 1

1 In the **Model Builder** window, click **Size 1**.

2 In the **Settings** window for **Size**, locate the **Element Size** section.

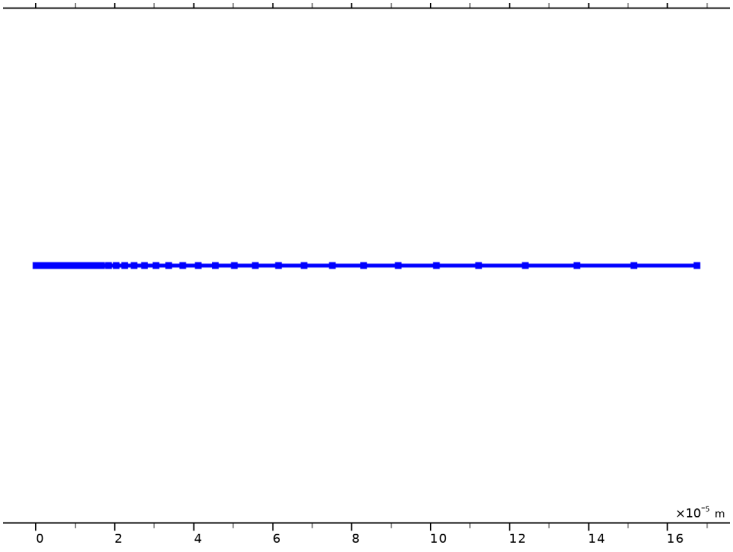
3 Click the **Custom** button.

4 Locate the **Element Size Parameters** section.

5 Select the **Maximum element size** checkbox. In the associated text field, type `L/10000`.

Edge 1

In the **Model Builder** window, right-click **Edge 1** and choose **Build All**.



STUDY 1

The model is now ready for solving. Add a parametric sweep to solve for three different sets of parameters.

Parametric Sweep

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
K_prime (Dimensionless adsorption-desorption rate constant ratio)	`1e5 1e-5 1e5`	

`K_prime` is a dimensionless parameter representing the ratio of the adsorption versus the desorption rate.

5 Click + **Add**.

6 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
k_0_prime (Dimensionless electron transfer rate constant)	`1e2 1e2 1e-2`	

`k_0_prime` is a dimensionless parameter representing the charge transfer rate constant.

With the above settings you will now compute and compare: 1) a base case, 2) a reaction limited by adsorption and 3) a case limited by slow charge transfer.

7 In the **Study** toolbar, click = **Compute**.

RESULTS

Cyclic Voltammograms (tcd)

The following will modify the automatically created voltammogram plot.

Global 1

1 In the **Model Builder** window, expand the **Cyclic Voltammograms (tcd)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, click to expand the **Legends** section.

Polish the legend as follows:

3 From the **Legends** list, choose **Evaluated**.

4 In the **Legend** text field, type `K'=eval(K_prime), k<sub>0</sub>'=eval(k_0_prime)`.

Compare the plot with Figure 1.

Surface Coverages and Concentration

Plot the surface coverages of A_ads and B_ads, as well as the electrolyte concentration of A, at the electrode surface for the three cases as follows:

1 In the **Results** toolbar, click **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Surface Coverages and Concentration` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 From the **Parameter selection (K_prime, k_0_prime)** list, choose **From list**.

5 In the **Parameter values (K_prime,k_0_prime)** list box, select **1: K_prime=1E5, k_0_prime=100**.

Point Graph 1

1 Right-click **Surface Coverages and Concentration** and choose **Point Graph**.

Select the leftmost boundary in the graphics window.

2 Select Boundary 1 only.

3 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Electroanalysis** > **Adsorbing–desorbing species** > **Surface coverage of adsorbing–desorbing species** > **tcd.theta_es1_A_ads - Surface coverage of adsorbing–desorbing species, 1-component**.

4 Click to expand the **Legends** section. Select the **Show legends** checkbox.

5 From the **Legends** list, choose **Manual**.

6 In the table, enter the following settings:

Legends
A_{ads}

7 In the **Surface Coverages and Concentration** toolbar, click **Plot**.

Point Graph 2

1 Right-click **Point Graph 1** and choose **Duplicate**.

2 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Electroanalysis** > **Adsorbing–desorbing species** > **Surface coverage of adsorbing–desorbing species** > **tcd.theta_es1_B_ads - Surface coverage of adsorbing–desorbing species, 2-component**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
B_{ads}

4 In the **Surface Coverages and Concentration** toolbar, click **Plot**.

Point Graph 3

1 Right-click **Point Graph 2** and choose **Duplicate**.

2 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Electroanalysis** > **Species c_A** > **c_A - Molar concentration, c_A - mol/m³**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
A

Surface Coverages and Concentration

To polish the title, y-axis settings and legend position, proceed as follows:

1 In the **Model Builder** window, click **Surface Coverages and Concentration**.

2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `K'=eval(K_prime), k<sub>0</sub>'=eval(k_0_prime).`

5 Locate the **Plot Settings** section.

6 Select the **y-axis label** checkbox. In the associated text field, type `Surface Coverage (1)`.

7 Select the **Two y-axes** checkbox.

8 In the table, select the **Plot on secondary y-axis** checkbox for **Point Graph 3**.

9 Locate the **Legend** section. From the **Position** list, choose **Upper middle**.

10 In the **Surface Coverages and Concentration** toolbar, click **Plot**.

Compare the plot with Figure 2.

11 Locate the **Data** section. In the **Parameter values (K_prime,k_0_prime)** list box, select **2: K_prime=1E-5, k_0_prime=100**.

12 In the **Surface Coverages and Concentration** toolbar, click **Plot**.

Compare the plot with Figure 3.

13 In the **Parameter values (K_prime,k_0_prime)** list box, select **3: K_prime=1E5, k_0_prime=0.01**.

14 In the **Surface Coverages and Concentration** toolbar, click  **Plot**.

Compare the plot with Figure 4.