

Application Note AN-EIS-009

# Mott-Schottky Analysis

## Using EIS for semiconductor applications

Semiconductors are intrinsic to modern life, but they stand to play an even greater role in the coming energy transition. Several techniques are employed in the pursuit of improved materials for energy production and storage. One particularly popular method for studying the electronic properties of potential new semiconducting materials is Mott-Schottky Analysis. The technique can be best understood as an extension of electrochemical impedance spectroscopy (EIS). By performing EIS at a range of different DC bias or offset potentials, the reciprocal of the square capacitance can be derived from the data and then plotted against

the DC offset itself, producing a so-called Mott-Schottky Plot. From such a plot, critical parameters such as the carrier concentration, the doping profile, and the flatband potential can be conveniently extracted.

This technique is popular across different fields, as it is versatile, non-destructive, and relatively fast. Compared to other options, Mott-Schottky Analysis also requires relatively little specialist equipment. This Application Note presents an example of Mott-Schottky measurement on a popular semiconducting material using VIONIC powered by INTELLO.

## INTRODUCTION

It is important to note that semiconductors exhibit quite different electrochemical behavior when compared to the traditional well-conducting electrode materials (e.g., glassy carbon or platinum). Namely, semiconductor electrochemistry is complicated by the appearance of a space charge region that extends from the surface into the material itself. During a Mott-Schottky measurement, it is the capacitance of the space charge region which is probed. This region is related to the redistribution of charge that occurs when the material is placed in contact with the electrolyte. The energy levels of the valence and conduction bands within the space charge region are distorted (a process called «band bending») so

that the fermi level of the semiconductor matches the redox potential of the electrolyte/redox system. The degree of band bending can be artificially adjusted using a potentiostat. Logically, there must be an applied potential where no band bending occurs – this is termed the «flatband potential» ( $E_{FB}$ ). This is a useful parameter that gives information about the energy levels within the semiconductor and how to best optimize the operating conditions of the semiconducting material.

It is possible to relate the flatband potential and also, conveniently, the doping density (carrier concentration) to the capacitance of the space charge region by the Mott-Schottky equation, shown here:

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_D} \left( E - E_{FB} - \frac{kT}{e} \right)$$

where  $\epsilon$  is the dielectric constant of the material,  $\epsilon_0$  ( $8.85E - 12 F m^{-1}$ ) is the vacuum permittivity,  $A$  (m) is the exposed area of the material,  $e$  ( $1.60E - 19 C$ ) is the electronic charge,  $N_D$  is the doping density,  $E$  is the applied DC offset,  $E_{FB}$  is the flatband potential,  $k$  ( $1.38E$

$- 23 J K^{-1}$ ) is the Boltzmann constant, and  $T$  (K) is the temperature.

It should be clear from the above that a plot of  $1/C_{SC}^2$  vs  $E$  allows both  $N_D$  and  $E_{FB}$  to be calculated from the slope and the intercept at the x-axis, respectively:

$$Intercept = E_{FB} + \frac{kT}{e}$$

$$Intercept - \frac{kT}{e} = E_{FB}$$

$$Slope = \frac{2}{\epsilon\epsilon_0 A^2 e N_D}$$

$$N_D = \frac{2}{\epsilon\epsilon_0 A^2 e Slope}$$

Note that EIS can be used to obtain the capacitance of the space charge region assuming that the chosen frequency is

sufficiently high (kHz), such that the following equations are true:

$$\frac{1}{C_s^2} = (-\omega Z'')^2$$

$$\frac{1}{C_p^2} = \left( \frac{(-Z''^2 + (Z' - R_s)^2 \omega)}{-Z''} \right)^2$$

where  $-Z''$  is the imaginary impedance,  $\omega$  is the angular frequency,  $R_s$  is the serial (uncompensated) resistance,  $1/C_s^2$  is the capacitance if modelled by a serial connection of

$R_s$ - $C_s$ , and  $1/C_p^2$  is the capacitance if modelled by a parallel connection of  $R_s$ - $C_p$  /  $R_p$ .

## SAMPLE AND SAMPLE PREPARATION

A 250 mL three-electrode cell was employed for this application study. As the working electrode, an FTO-coated (fluorine-doped tin oxide) glass slide (25 × 25 × 1 mm, RedoxMe) was used. The slides were washed with ultrapure water before use and then mounted on a sample holder (RedoxMe). The counter electrode consisted of

two Pt sheet electrodes shorted together to increase the overall surface area. (PT.SHEET, Metrohm). The reference electrode used was Ag/AgCl (6.0733.100, Metrohm). The electrolyte (0.1 mol/L NaCl) was not purged and was exposed to the ambient air.

## EXPERIMENTAL

Electrochemical impedance spectroscopy was first carried out at 0 V (vs. reference) with a frequency range of 100 kHz to 0.1 Hz. This was done in order to ensure the validity of the setup, and to determine  $R_S$  (the uncompensated resistance). Following this, Mott-Schottky analysis was conducted by measuring impedance spectra over a range of DC offsets (from 0 to 1 V, in 0.1 V steps). For each DC offset, the value of the imaginary impedance at 1000

Hz was extracted and used to calculate the reciprocal of the square capacitance from the above equations, which was then plotted against the different DC offsets.

VIONIC powered by INTELLO was used to complete the measurement and collect the data. The default Mott-Schottky procedure in INTELLO 1.5 can be used. Analysis of the results was accomplished with the NOVA software.

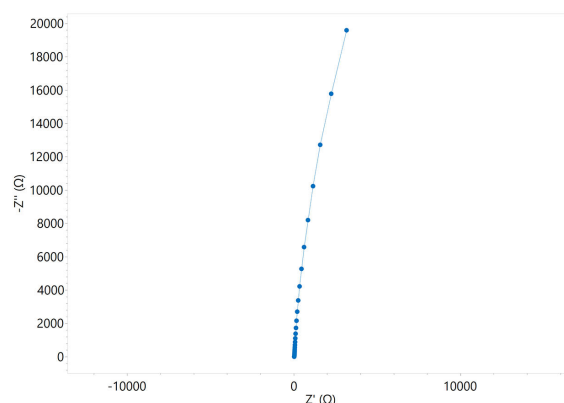
## RESULTS

In **Figure 1**, the complete Nyquist plot collected at 0 V is shown. The plot is dominated by the capacitance of the sample [1]. Using the Fit and Simulation tool in NOVA, it is possible to calculate the uncompensated resistance as 29.9  $\Omega$ . The data is fitted to an R-R/C circuit.

The Mott-Schottky plot is built in NOVA using the Windower and Calculate Signal commands shown in **Figure 2**.

The resulting Mott-Schottky plot (**Figure 3**) exhibits a positive slope in this potential range, indicating n-type conductivity.

In NOVA, a regression analysis was performed between 0 and 1.1 V Ag/AgCl in order to obtain the slope of the plot (b in **Figure 4**), and by extrapolation to  $y = 0$ , the crossing at the x-axis.

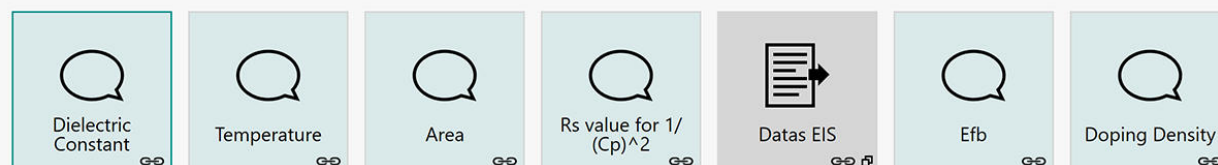


**Figure 1.** Nyquist plot of the FTO-coated sample in 0.1 mol/L NaCl.

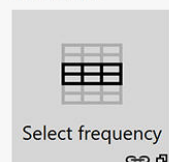
## DATA

INTELLO 1.4 - Canned Demo - Mott-Schottky (Calculations Included) - Data (15/06/2023 09:32)

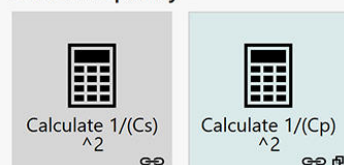
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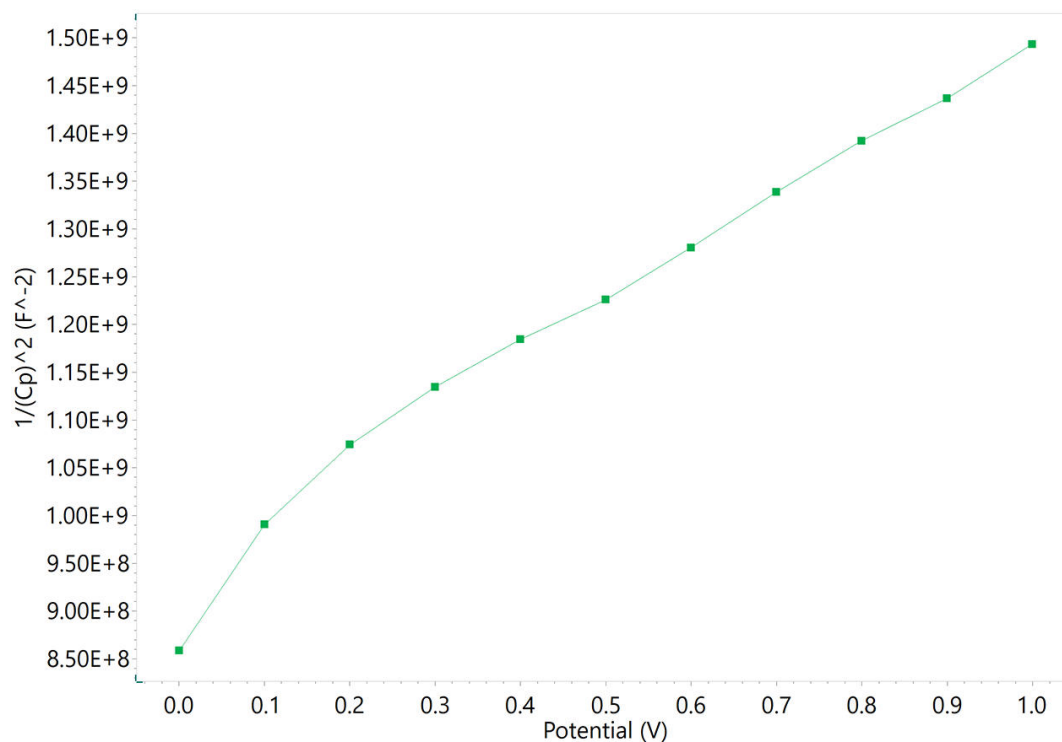
### Datas EIS



### Select frequency



**Figure 2.** Data analysis commands within NOVA used to build a Mott-Schottky plot.



**Figure 3.** Mott-Schottky plot of the FTO-coated sample in 0.1 mol/L NaCl.



## Results

Function description  $y = 927320000 + 583180000x$   
 Correlation coefficient 0.98964  
 a 9.2732E+08  
 b 5.8318E+08  
 1/Slope 1.7147E-09

**Figure 4.** Results of the regression analysis.

$$\text{When } y = 0, x = E_{FB} + \frac{kT}{e}$$

$$y = a + bx$$

$$0 = a + bx$$

$$0 - a = bx$$

$$\frac{-a}{b} = x$$

$$\frac{-a}{b} = E_{FB} + \frac{kT}{e}$$

$$\frac{-a}{b} - \frac{kT}{e} = E_{FB}$$

From these results and the equations above, the flatband potential was determined from the intercept as -1.61 V (vs. 3 mol/L Ag/AgCl or -1.40

V vs. SHE). Comparable values have been reported for FTO in the literature [2].

$$N_D = \frac{2}{\epsilon\epsilon_0 A^2 e \text{Slope}}$$

Assuming the dielectric constant is also known (here taken as 2.137 from [3]), the doping density can be calculated from the slope using

the previous equation as  $2.90 \times 10^{21} \text{ cm}^{-3}$ . This is also comparable to the doping densities reported in scientific literature [1,3].

## CONCLUSIONS

In this Application Note, an example Mott-Schottky measurement is shown using VIONIC powered by INTELLO. The flatband potential and

doping density have been calculated using NOVA and are comparable to values for this type of sample found in the literature.

## REFERENCES

1. Korjenic, A.; Raja, K. S. Electrochemical Stability of Fluorine Doped Tin Oxide (FTO) Coating at Different pH Conditions. *J. Electrochem. Soc.* **2019**, *166* (6), C169–C184.  
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3. Sanz-Navarro, C. F.; Lee, S. F.; Yap, S. S.; et al. Electrochemical Stability and Corrosion Mechanism of Fluorine-Doped Tin Oxide Film under Cathodic Polarization in near Neutral Electrolyte. *Thin Solid Films* **2023**, *768*, 139697.  
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## CONFIGURATION



### VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new INTELLO software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage:  $\pm 50$  V
- Standard current  $\pm 6$  A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1  $\mu$ s

Also included in VIONIC's price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan