8 Appendix

8.1 X-ray diffraction of cobalt nanoparticles

Cobalt sample was examined by X-ray diffraction in reflection mode with the cobalt $k_{\alpha}$ ($\lambda = 1.788$ Å) radiation. The result obtained at wide diffraction angles is showed on the following graphs.

![XRD spectrum of cobalt nanoparticles deposited from aqueous solution (a) or in the presence of Brij 76 liquid crystal (b) within the pores of alumina membrane.](image)

Fig. 8.1. XRD spectrum of cobalt nanoparticles deposited from aqueous solution (a) or in the presence of Brij 76 liquid crystal (b) within the pores of alumina membrane.

The spectrum exhibits interesting features, showing the main diffraction peaks at $2\theta \sim 44.9$, 52.4 and 77.4° characteristic of the aluminum substrate. Two other peaks appear at 48.8 and 55.85° characteristic of (100) and (101) diffraction plan of hexagonal centered (hcp) cobalt with
reticular distances 2.165 and 1.910 Å respectively. Another signals centered around 52° and 61° are detected, thus including the presence of face-centered-cubic (fcc) cobalt particles with $d_{111}$ and $d_{200}$ of 2.047 and 1.77 Å respectively. Both hexagonal and cubic cobalt crystals are present in the pore of alumina membrane; the broadening of the XRD peaks is indicative of the nanoparticles.

8.2 Phase diagram of surfactant used in double template deposition.

![Phase diagram](image)

Fig. 8.2. Liquid crystal phase behavior of CTAB + water mixture. Copy from reference [38] page 19

The composition of the CTAB hexagonal mixture used in this investigation was chosen according to the giving phase diagram. A large hexagonal domain ($H_1$) dominates the phase diagram of CTAB mixture.
The composition of the hexagonal phase of Brij 78 liquid crystal mixture used in this investigation was choose according to the given phase diagram and check with small angle x-ray scattering. The Brij 78 plating mixture is simpler in behavior and the hexagonal domain ($H_1$) is stable over a large temperature and composition range.

### 8.3 Working hypothesis for impedance measurement

The electrochemical impedance spectroscopy can provide useful information only when the investigation is performed correctly. For a successful experiment, some basic requirements are needed, among other we have:

- **The linearity**: the responses of the input sinusoidal voltage should be a sinusoidal current with the same frequency, different phase and amplitude. This is achieved experimentally if the amplitude of the sine wave perturbation signal is small enough to keep the selected state of the system unchanged.

- **Lack of convection and migration**: no changes in local concentration of electrolyte other than those caused by diffusion or charge transfer should occur.

- **Single input - single output**: this requirement could be achieved if the parameters such as temperature, concentration, and pH are kept constant.

- **Steady state**: The system being measured must be at a steady state throughout the time required to measure. In practices the cell can change through adsorption of solution impurities, grow of an oxide layer, coating degradation and temperature changes [69, 72].
Fig. 8.4. Potential input and current output recorded during potentiodynamic EIS (for Mott-Schottky analysis). (a) good current response, (b) bad current response of the ac voltage.

The system (a) is linear because the current response of the voltage is also a sinusoidal function of the same frequency, different phase and amplitudes. On the contrary, the current response in (b) is not very good. The system (b) doesn’t obey to all working hypothesis and the result obtained with such signal response should not be valid.

8.4 Fitting of impedance data and calculation of the $Z(j\omega)$ equations.

8.4.1 Impedance of alumina membrane.

Fig. 8.5. Nyquist representation of impedance data of aluminum oxide anodized at 10°C fitted with the equivalent Circuit. “Msd” and “Calc” refer to measured and calculated data, respectively.
The real and imaginary part of impedance was calculated as function of the frequency of the sinusoidal voltage.

**Recall** (From Ref. [69], [71], [101] &[152])


**De Moivre theorem of complex number [152].**

\[
[r \cos(\theta) + j \sin(\theta)]^p = r^p \left[ \cos \left( \frac{p}{q} \theta \right) + j \sin \left( \frac{p}{q} \theta \right) \right]
\]

That is the power of a complex number written in the trigonometric form; \( r \) is the module of the complex number and \( \theta \) its argument.

Therefore, \( j^p = \cos \frac{\pi}{2} + j \sin \frac{\pi}{2} \), \( j^{-p} = \cos \frac{\pi}{2} - j \sin \frac{\pi}{2} \) and \( \sqrt{j} = \frac{1}{2} \cos \frac{\pi}{2} + j \sin \frac{\pi}{2} = \frac{\sqrt{2}}{2} + j \frac{\sqrt{2}}{2} \)

**Euler relations**

\[
e^{j\theta} = \cos \theta + j \sin \theta \quad \text{and} \quad e^{-j\theta} = \cos \theta - j \sin \theta
\]

- Association of resistors in series.

\[
R_{eq} = R_1 + R_2 + \ldots + R_n
\]

- Association of resistor in parallel:

\[
\frac{1}{R_{eq}} = \frac{1}{R_1} + \frac{1}{R_2} + \ldots + \frac{1}{R_n}
\]

Impedance of a capacitor:

\[
Z_c = \frac{1}{j\omega C}
\]

Impedance of a constant phase element (CPE or Q): \( Z_Q = \frac{1}{A(j\omega)^{\alpha}} \)

Warburg element (W):

\[
Z_W = \frac{\sigma}{\sqrt{j\omega}}
\]

For any angle \( \theta \), \( \cos^2 \theta + \sin^2 \theta = 1 \)

These relations can be used to calculated the impedance expression of porous alumina.
The calculation was done according to the following rule: when the elements are connected in series, their impedance are added to each other; while in the case of parallel connection, their admittances or the reciprocal of the impedances are added \([69]\). For clarity, the subscript \(Q\) was used in equations to refer for constant phase element instead of the symbol “CPE” shown in the model.

\[
Z(j\omega) = R_s + Z_1 \quad \text{Where } Z_1 \text{ is the equivalent impedance of the parallel part of the model.}
\]

\[
\frac{1}{Z_1} = \frac{1}{R_p} + \frac{1}{Z_Q} = \frac{1}{R_p} + \frac{A\omega^a}{\cos \alpha \pi/2 - j\sin \alpha \pi/2} = \frac{\cos \alpha \pi/2 - j\sin \alpha \pi/2 + AR_p\omega^a}{R_p(\cos \alpha \pi/2 - j\sin \alpha \pi/2)}
\]

\[
Z_1 = \frac{R_p(\cos \alpha \pi/2 - j\sin \alpha \pi/2)}{AR_p\omega^a + \cos \alpha \pi/2 - j\sin \alpha \pi/2}
\]

It can be written in the form \(Z_1 = a + jb\) by multiplying and dividing by the conjugated expression of the denominator.

\[
Z_1 = \frac{R_p(\cos \alpha \pi/2 - j\sin \alpha \pi/2)(AR_p\omega^a + \cos \alpha \pi/2 + j\sin \alpha \pi/2)}{(AR_p\omega^a + \cos \alpha \pi/2 - j\sin \alpha \pi/2)(AR_p\omega^a + \cos \alpha \pi/2 + j\sin \alpha \pi/2)},
\]

After development and simplification using \(\cos^2\theta + \sin^2\theta = 1\), we obtain

\[
Z_1 = \frac{R_p + R_p^2 A\omega^a(\cos \alpha \pi/2 - j\sin \alpha \pi/2)}{1 + R_p^2 A\omega^a + 2R_p A\omega^a \cos \alpha \pi/2}
\]

therefore \(Z(j\omega) = R_s + Z_1\)
\[ Z(j\omega) = R_s + \frac{R_p + R_p^2 A\omega^a (\cos\alpha \frac{\pi}{2} - j\sin\alpha \frac{\pi}{2})}{1 + R_p^2 A^2 \omega^{2a} + 2 R_p A\omega^a \cos\alpha \frac{\pi}{2}} \]  

(20)

The real and the imaginary parts of the impedance appear clearly on the mathematical expression.

8.4.2 Impedance of cobalt film deposited from aqueous solution into AAO.

As shown by the figure, the equivalent model is in agreement with the experimental data. The same principle as in the cases of porous alumina was used to establish the mathematical expression of the impedance of this system as function of frequency.

\[ R_s \text{ is in series with the second part of the model, therefore } Z(j\omega) = R_s + Z_1, \text{ where} \]

\[ \frac{1}{Z_1} = \frac{1}{Z_Q} + \frac{1}{Z_2} \text{ and } Z_2 = R_p + Z_w \]
. Calculation of $Z_2$

$$Z_2 = R_p + \frac{\sigma}{\sqrt{j \omega}} = R_p + \frac{\sigma}{\sqrt{j \omega}} e^{\frac{j \pi}{4}} = R_p + \frac{\sigma}{\sqrt{j \omega}} e^{\frac{j \pi}{4}} = R_p + \frac{\sigma}{\sqrt{j \omega}} e^{-\frac{j \pi}{4}}$$

- Calculation of $Z_1$

$$\frac{1}{Z_1} = \frac{1}{A(j \omega)^{\alpha}} + \frac{1}{R_p + \frac{\sigma}{\sqrt{j \omega}} e^{-\frac{j \pi}{4}}} = A\omega^{\alpha} (\cos \frac{\pi}{2} + j \sin \frac{\pi}{2}) + \frac{1}{R_p + \frac{\sigma}{\sqrt{j \omega}} e^{-\frac{j \pi}{4}}} = A\omega^{\alpha} e^{\frac{j \pi}{2}} + \frac{1}{R_p + \frac{\sigma}{\sqrt{j \omega}} e^{-\frac{j \pi}{4}}}$$

After reduction to the same denominator and rearrangement, we obtain

$$Z_1 = \frac{R_p \sqrt{\omega} + \sigma e^{-\frac{j \pi}{4}}}{A\omega^{\alpha} e^{\frac{j \pi}{2}} \left( R_p \sqrt{\omega} + \sigma e^{-\frac{j \pi}{4}} \right) + \sqrt{\omega}}$$

The total impedance expression can be written by replacing $Z_1$ in $Z(j \omega) = R_s + Z_1$

$$Z(j \omega) = R_s + \frac{R_p \sqrt{\omega} + \sigma e^{-\frac{j \pi}{4}}}{A\omega^{\alpha} e^{\frac{j \pi}{2}} \left( R_p \sqrt{\omega} + \sigma e^{-\frac{j \pi}{4}} \right) + \sqrt{\omega}} \quad (22)$$

Because of the complexity of the mathematical expression, $Z(j \omega)$ was not decomposed into real and imaginary part.

8.4.3 Impedance of cobalt film deposited from Brij 76 liquid crystal into AAO

![Graph showing impedance of cobalt deposited from Brij 76 fitted with the equivalent model.](image)

Fig. 8.7. Impedance of cobalt deposited from Brij 76 fitted with the equivalent model.
The experimental (measured Msd) and calculated (calc) data are in agreement. In this last case the electrical model is as follow.

We should remark that the first part of the model is similar to that of the sample deposited from aqueous solution.

\[ Z(j\omega) = R_s + Z_1 + Z_3 \]

\( Z_1 \) has the same expression as in the last case, only \( Z_3 \) will be calculated.

- **Calculation of** \( Z_3 \)

\[ \frac{1}{Z_3} = \frac{1}{R} + \frac{1}{Z_q' + A(j\omega)'} = \frac{1}{R} + A'\omega^{\alpha'} e^{j\alpha'\frac{\pi}{2}} = \frac{1}{R} + A'\omega^{\alpha'} e^{j\alpha'\frac{\pi}{2}} \]

from there

\[ Z_3 = \frac{R}{1 + A'\omega^{\alpha'} e^{j\alpha'\frac{\pi}{2}}} \]

The total impedance expression can be written as follow:

\[ Z(j\omega) = R_s + \frac{R_p\sqrt{\omega} + \sigma e^{-j\frac{\pi}{4}}}{A\omega^{\alpha} e^{j\alpha\frac{\pi}{2}} + \sqrt{\omega}} + \frac{R}{1 + A'\omega^{\alpha'} e^{j\alpha'\frac{\pi}{2}}} \] (23)
8.4.4. Impedance model of alloys nanoparticles.

Fig. 8.8. Impedance of NiCu alloy nanofilm deposited from liquid crystal. Msd and Calc refer to experimental and calculated data respectively. The electrical model is in good agreement with the experimental.

The first part of the model is similar to that of sample deposited from aqueous solution into AAO. The total impedance of this model can be written as:

$$Z(j\omega) = R_s + Z_1 + Z_4$$

where $Z_1$ is the same as in the last case, only $Z_4$ will be calculated.

**Calculation of $Z_4$**

$$\frac{1}{Z_4} = \frac{1}{j\omega C} + \frac{1}{R_{po}} + \frac{1}{R_p} = \frac{1 + jC\omega R_{po}}{R_{po}}$$

From this expression we obtain
The general impedance equation can be written as function of frequency as follow.

\[
Z_4 = \frac{R_{po}}{1 + jC\omega R_{po}}
\]

More information’s about the calculation of model impedance as well as examples of calculated models can be found in references [69] and [71].

**8.5. Principle of the Atomic Force Microscopy (AFM)**

In AFM, the force between the tip and the sample surface cause the cantilever to bend or deflect. Several forces contributed to the deflection of the AFM cantilevers, but the most common force associated with AFM is the inter-atomic force called the Van der Waals force.

\[
Z(j\omega) = R_s + \frac{R_p\sqrt{\omega} + \sigma e^{-j\frac{\pi}{4}}}{A\omega^\alpha e^{j\frac{\pi}{4}}\left(R_p\sqrt{\omega} + \sigma e^{-j\frac{\pi}{4}}\right) + \sqrt{\omega}} + \frac{R_{po}}{1 + jC\omega R_{po}}
\]

Fig. 8.9. Interatomic force vs distance curve, scanned from reference [65].
Fig. 8.9 shows the dependence of the Van der Waals force on the distance between tip and the sample. In the contact regime, the cantilever is held very close to the sample, and the inter-atomic force between the cantilever and the sample is repulsive. In the non-contact regime, the cantilever is held on the order of tens to hundreds of angstroms from the samples surface and the inter-atomic force between the cantilever and the sample is attractive.


In most common AFM instrument, a laser beam bounces off the back of the cantilever onto a position-sensitive photo detector (PSPD). As the cantilever bends, the position of the laser beam on the detector shifts. The PSPD can measure displacements of light as small as 10 Å. The measured cantilever deflections allow the computer to generate the map of the surface topography.