Solid-State Electrochemistry

1.3.3 – Diagram for MX_2 crystal

The diagram is obtained by plotting in logarithmic coordinates the variation in concentration of each species as a function of partial pressure P_{X_2} and at a given temperature. We can distinguish two cases: $K_{AF} \gg K_e$ and $K_e \gg K_{AF}$. Figure 2 shows the form of the Brouwer diagram for the compound MX_2 for $K_{AF} \gg K_e$. Note that, in the intermediate domain, a plateau appears coinciding with the dominance of atomic structure defects. This domain must not be confused with the domain of redox stability or with the domain of crystal ionicity (see fig. 41, page 98).

Elsewhere, the concentrations of all the species vary with P_{X_2}. Point S is defined in section 1.4.

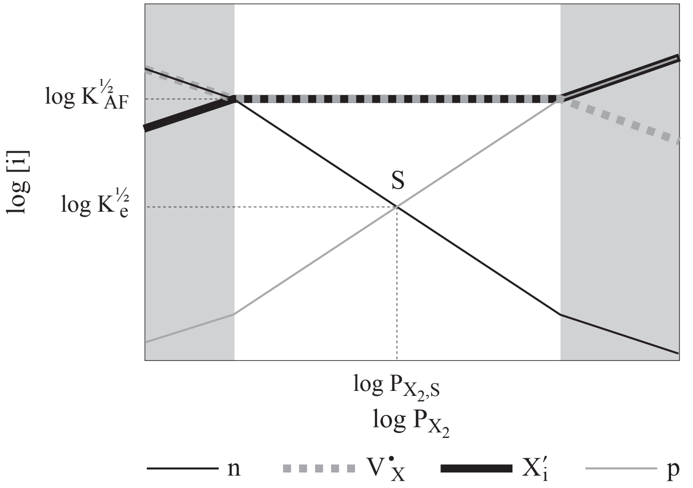

Figure 2 – Brouwer diagram for pure MX_2 compound at temperature T.

1.3.4 – Case of solid solution $(MX_2)_{1-x}(DX)_x$

We now treat the case where D is substituted for M. The reaction that substitutes DX for MX_2 is $DX \longrightarrow D_M' + X_X^{\times} + V_X^{\bullet}$

We observe an increase in the rate of $V_X^{\bullet}$ vacancies of extrinsic origin. For typical doping levels (several %), the rate of extrinsic vacancies dominates that of the intrinsic vacancies. Under these conditions, the electroneutrality relation is

$$n + [X_i'] + [D_M'] = p + [V_X^{\bullet}] \qquad \text{where } [D_M'] = \text{const.}$$

2.1.5 – Physical meaning of complex impedance spectra

By analogy with electric circuits, complex impedance spectra provide the following information for a conducting material:

- ▹ $\mathrm{Re}(Z)_{\max} = R$: sample resistance. Its conductivity σ is obtained from

  $$\sigma = \frac{1}{R} \times \frac{\ell}{S}$$

  where ℓ and S are the sample thickness and surface area, respectively.
- ▹ $\mathrm{Im}(Z)_{\max}$ is the maximum phase shift. The equivalent capacitance C is obtained from

  $$C = \varepsilon_0 \varepsilon_R \frac{S}{\ell}$$

  where ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.8542 \times 10^{-12}\ \mathrm{F\,m^{-1}}$) and ε_R is the dielectric constant (or relative permittivity) of the sample.

The impedance spectra of ceramics generally show three domains, as shown in figure 15. Phenomena associated with grains appear at high frequencies, those associated with the microstructure (grain boundaries) appear at intermediate frequencies, and those associated with the electrode reaction appear at low frequencies.

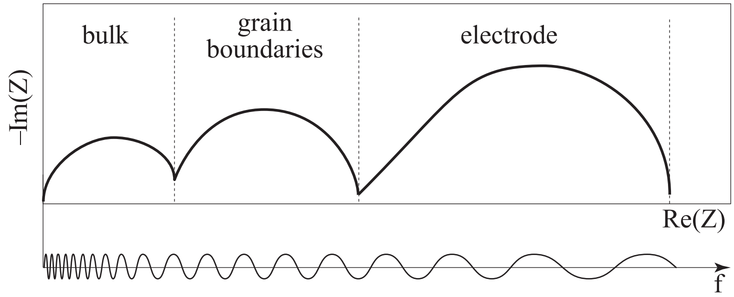

Figure 15 – General form of impedance spectrum for a ceramic.

2.2 – Methods to measure transport number

2.2.1 – Electromotive force method

The presentation of this method is based on the mixed conductor (ionic + electronic) described by the formula MX (M^+X^-). Consider the following electrochemical chain:

$$\mathrm{Me}/\mu_X^{(1)}|\mathrm{MX}|\mu_X^{(2)}/\mathrm{Me}$$

Exercises

Exercise 2.1 – Determination of conductivity by four-electrode method

The four-electrode method, which is depicted schematically in figure 21, is used to determine the electrical conductivity of the electrode material $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ in air at various temperatures.

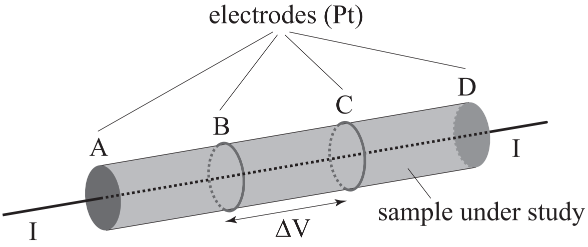

Figure 21 – Schematic diagram showing principle of four-electrode method.

The direct current is imposed in galvanostatic mode. The results obtained at 666 °C are listed in table 11.

Table 11 – Current at various potential differences between points B and C.

I [mA]	50	100	150	200	250	300	400	500
$V_B - V_C$ [mV]	2.11	4.22	6.33	8.44	10.55	12.66	16.88	21.09

1. Show that the sample obeys Ohm's law in the range of potential under study.

2. Determine the resistance $R_{B\text{-}C} = R_1$ between points B and C.

3. Given that the sample is cylindrical with a geometric factor $k = 7.59\ cm^{-1}$, what is the conductivity of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ at 666 °C?

4. Based on the resistance $R_{B\text{-}C}$ obtained at different temperatures (table 12),
   - **a.** plot the conductivity σ for $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ in the form $\log \sigma T = f(1/T)$;
   - **b.** deduce the activation energy in eV.

Solutions to exercises

Solution 2.1 – Determination of conductivity by four-electrode method

1. Figure 27 shows the potential difference $V_B - V_C$ as a function of the current I passing through the cell. The curve is linear and is given by

$$V_B - V_C = 0.0422 \times I$$

with $V_B - V_C$ in mV and I in mA.

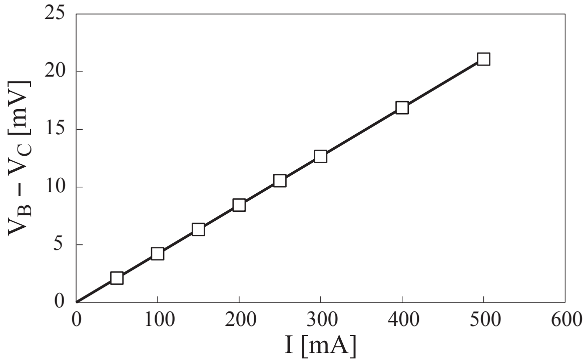

Figure 27 – Potential difference $V_B - V_C$ as a function of current I.

This linear variation indicates that $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ is ohmic under the given measurement conditions.

2. The resistance R_1 between points B and C corresponds to the slope of the line and is given by $R_1 = 0.0422\ \Omega$

3. The conductivity of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ is given by the relation

$$\sigma = \frac{k}{R} = \frac{7.59}{0.0422}$$

$$\sigma = 179.9\ \mathrm{S\,cm^{-1}}$$

4. a. Table 18 gives the data required to plot the conductivity in the form $\log \sigma T = f(1/T)$.

a. show that we obtain the solution

$$X_i = X^0 + \frac{I}{2FS\sqrt{j\omega D}}$$

b. deduce the expression for the overpotential η.

4. Starting from the derivative of the overpotential with respect to I near the origin ($I \approx 0$), or by doing a polynomial approximation

a. Show explicitly that the impedance obtained is a Warburg impedance.

Data

$$j^{-\frac{1}{2}} = \frac{1}{\sqrt{2}}(1-j)$$

b. For a symmetric cell containing two identical oxygen-diffusion-limited electrodes deposited on each side of a sintered solid, draw the general form of the impedance diagram in both the Nyquist and Bode representations. Represent and explain the different elementary contributions of the response of the electrochemical cell.

c. How does a point of fixed frequency evolve as a function of oxygen pressure in the gas surrounding the electrode material?

Exercise 4.2 – Study of oxygen-electrode reaction

We use impedance spectroscopy to study the electrochemical behavior of the lanthanum cobaltite $La_{0.7}Sr_{0.3}CoO_{3-\delta}$. Circular electrodes are deposited in a symmetric configuration on an yttria-stabilized zirconia (YSZ) electrode by radiofrequency sputtering. They have a diameter d = 20 mm and a thickness $\ell = 0.35\ \mu m$. The electrochemical cell is inserted in a tube furnace. Each electrode is connected to a frequency response analyzer (FRA) *via* platinum meshes and wires. A schematic diagram of the cell appears in figure 69.

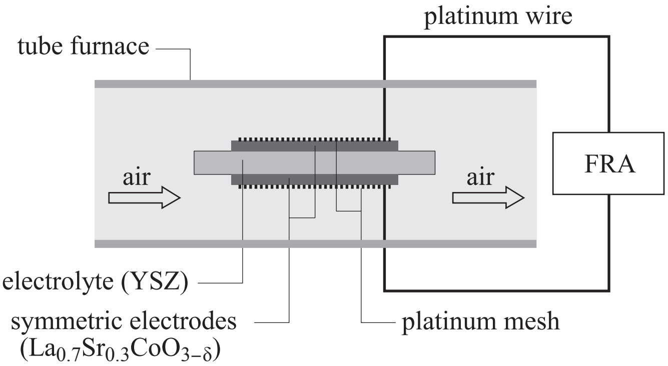

Figure 69 – Schematic diagram of cell and experimental setup.

Figure 70 shows the impedance diagram obtained in air after stabilization at 425 °C in the frequency range of $10^4 - 10^{-3}$ Hz.

This diagram is modeled by the equivalent electric circuit shown in figure 70. For high frequencies (f > 100 Hz), the model consists of an inductance L and the circuit $(R\,//\,CPE)_1$. At low frequencies (f < 100 Hz), the model consists of the circuit $(R\,//\,CPE)_2$ and at very low frequencies (f < 0.5 Hz) the model consists of a Warburg-type diffusion-limited element whose impedance is

$$Z(\omega) = A \times \frac{\tanh\sqrt{\tau j\omega}}{\sqrt{\tau j\omega}} \tag{1}$$

where ω is the frequency of the electric field, and A and τ are adjustable parameters. The complete expression for Warburg diffusion-limited impedance is

$$Z(\omega) = \frac{RT}{n^2F^2} \times \frac{\delta}{C^0 D} \times \frac{\tanh\sqrt{j\omega\frac{\delta^2}{D}}}{\sqrt{j\omega\frac{\delta^2}{D}}} \tag{2}$$

where δ is the thickness of the diffusion layer, D is the diffusion coefficient, C^0 is the interfacial concentration of the electroactive species, T is the absolute temperature, and n is the number of electrons exchanged in the electrochemical reaction in question. We consider only the low-frequency range (f < 100 Hz).

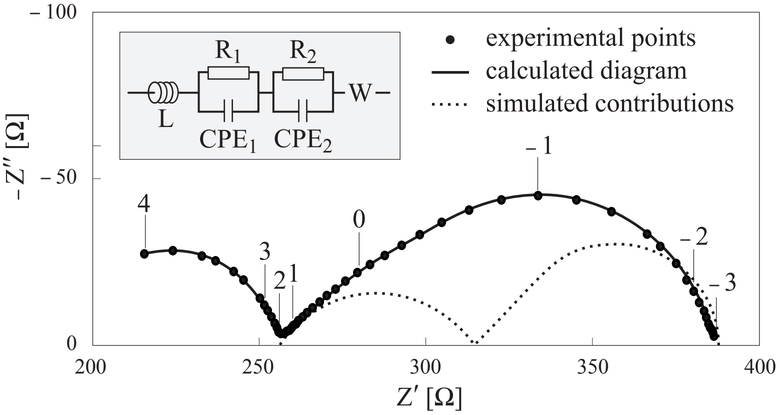

Figure 70 – Impedance diagram obtained under air after stabilization at 425 °C (from Ringuedé & Guindet, 1997).

By a least squares fit of the theoretical model (for the electrode reaction) to the experimental points, we determine the parameters given in table 39.

Chapter 5

Applications

Course notes

5.1 – Electrochemical sensors

5.1.1 – Definition and characteristics

An electrochemical sensor is a device that is capable of detecting variations in quantities related to a chemical species in a given phase (e.g., concentration, partial pressure, molar fraction). Such sensors generally consist of an active layer that can recognize and interact with the species and that is associated with a transducer capable of transforming the interaction into an electrical signal. The signal may be potentiometric, amperometric, conductometric, … The quantities measured are the concentrations (activities) of ionic species (H_3O^+, Na^+, Cl^-) and the partial pressures of gaseous species (O_2, H_2, CO_2, H_2O vapor, …).

Electrochemical sensors fulfill sufficiently well the requisite conditions in terms of stability, selectivity, response time, and reversibility. On the practical and economic level, they are robust, simple, inexpensive, convenient, and have an acceptable lifetime. They are used in particular for

- industrial-process engineering: metallurgy, plastics processing;
- the environment: analysis of effluents, water, soil, and air;
- automobile industry: battery charge level, analyze exhaust gas;
- medicine: diagnostics;
- security: leaks of toxic or noxious gases.

Data

Material	TiS_2	$LiTiS_2$
a [Å]	3.407	3.455
c [Å]	5.697	6.195

Exercise 5.6 – Chlorine sensor based on doped strontium chloride

A – Study of strontium chloride $SrCl_2$

Figure 85 shows the conductivity in Arrhenius coordinates of pure $SrCl_2$ and of $SrCl_2$ doped by KCl.

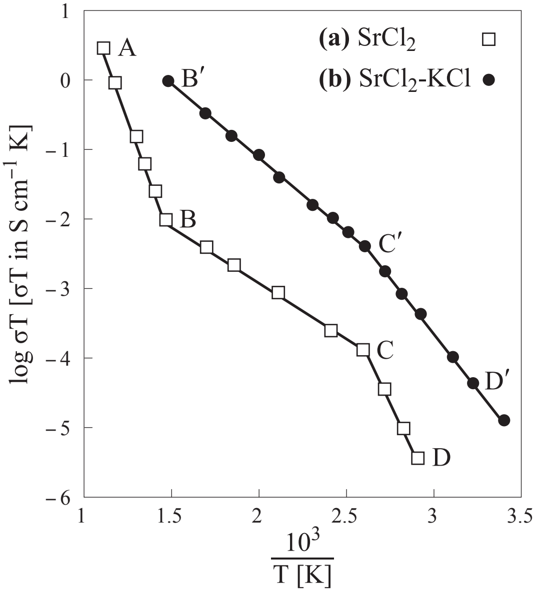

Figure 85 – Conductivity in Arrhenius coordinates of **(a)** pure $SrCl_2$ and **(b)** $SrCl_2$ doped with potassium chloride KCl.

1. Given that the dominant disorder is anionic Frenkel disorder,
   a. Write the equilibrium for structure defects involved and the associated equilibrium constant K_{AF}. The expression for this constant as a function of temperature is

$$K_{AF} = 9 \times 10^{-4} e^{-\frac{1.6\,eV}{kT}}$$

   b. Identify the various temperature domains that appear in figure 85(a).

c. The strontium is supposedly immobile. The electrochemical mobilities of the mobile species $V_{Cl}^{\bullet}$ and Cl_i' are given by

$$\tilde{u}_{V_{Cl}^{\bullet}} = \frac{6 \times 10^{-3}}{T} e^{-\frac{0.4\,eV}{kT}}$$

$$\tilde{u}_{Cl_i'} = \frac{36}{T} e^{-\frac{1\,eV}{kT}}$$

At what temperature do the two species have the same mobility?

d. Given that the conductivity of particle i is given by

$$\sigma_i = z_i^2 F^2 \tilde{u}_i [i]$$

▹ express the total conductivity of $SrCl_2$ for the conditions given in question 1(c) and assuming that it is purely ionic.

▹ Calculate the total conductivity.

2. a. Write the dissolution reaction for KCl in $SrCl_2$ given that the potassium substitutes for strontium.

b. Identify the various temperature domains that appear in figure 85(b).

3. a. Make qualitative Brouwer diagrams of pure $SrCl_2$ and of the solid solution $SrCl_2$-KCl with “a” denoting the doping level.

b. Justify the use of the solid solution $SrCl_2$-KCl as electrolyte for making a chloride sensor.

4. We introduce silver chloride AgCl into the solid solution $SrCl_2$-KCl.

a. Write the reaction for doping the solid solution $SrCl_2$-KCl with silver chloride AgCl. We assume that silver occupies interstitial positions and that chlorine occupies normal positions.

b. Denote by b the concentration of AgCl in the resulting solid solution. Express the total ionic conductivity σ_t' for the case where $b = a = \sqrt{K_{AF}}$ and taking into account the identical mobilities of $V_{Cl}^{\bullet}$ and Cl_i'.

c. Calculate σ_t' for these conditions.

Data

$$\tilde{u}_{Ag^+} = \frac{6 \times 10^2}{T} e^{-\frac{1\,eV}{kT}}$$

B – Study of chlorine sensor

We consider the following isothermal electrochemical chain:

$$\underset{(1)}{Cl_2(P_1),Me} \;/\; SrCl_2\text{-}KCl \;/\; \underset{(2)}{Me,Cl_2(P_2)}$$

where P_1 and P_2 denote the partial pressure of chlorine at electrodes (1) and (2), respectively.

1. Write the electrochemical reaction at the electrodes.

2. With the help of the electrochemical potentials of the species involved, derive the expression relating the emf at the chain terminals to the chlorine partial pressure and to the temperature.

3. We build the sensor shown schematically in figure 86 where ruthenium dioxide RuO_2 is an electronically conducting catalyst. Ag and AgCl are distinct solid phases.
   - **a.** Derive the expression relating the emf at the chain terminals to the chlorine partial pressure.
   - **b.** Specify the role of the Ag-AgCl mixture.

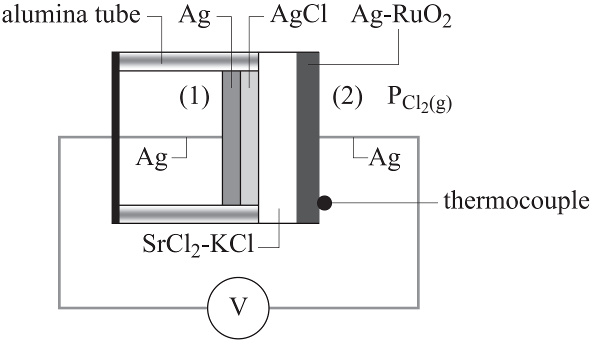

Figure 86 – Schematic representation of a chlorine sensor (from Déportes *et al.*, 1994).

4. Table 48 gives the sensor emf as a function of temperature for a Cl_2 partial pressure of 1 bar.

Table 48 – emf of chlorine sensor as a function of temperature for a Cl_2 partial pressure of 1 bar.

T [°C]	115.5	165.7	203.2	262.4	311.7	376.7	434.9
emf [mV]	1 100.0	1 070.4	1 044.0	1 010.2	978.5	941.5	909.9

   - **a.** Plot the emf as a function of absolute temperature T and deduce the relationship $\Delta E = f(T)$.