

INTRODUCTION TO THE SCALING PROPERTIES IN ELECTRO-CHEMISTRY: FROM THE "TEISI" MODEL TO THE LITHIUM FRACTAL ORDERING IN Li_xFeS_2 LAYERED STRUCTURE

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Summary

Attention is drawn to the generalisation to the fractal geometry of the relations which control the interfacial energy and mass exchange in the linear approximation.

From this kinetic analysis the solid state motion of lithium in Li_xFeS_2 is shown to be related to the fractal ordering of this ion in the lattice.

Scaling phase transitions are pointed out.

Li_xFeS_2 [1] is a very interesting member of the group of layered compounds available for the solid state electrochemical reduction through lithium insertion in the van der Waals gap, when understanding the kinetic differences of the ionic motion both in the single- and in the two-phase states. Indeed, this non-stoichiometric compound shows two major domains, the first being diphased ($0.14 < x < 1.09$) and the second being monophased ($1.09 < x \leq 2$), with a slight first order electronic transition in the middle of the monophased domain ($x \cong 1.5$) [2, 3].

In this latter case, the electrochemical limitations arise from dissipative diffusion control, but the nature of the motion through the two-phase state is unknown because of the lack of fit with diffusion theory [4].

Therefore in order to understand the motion of the poor/rich ionic interface through the reduction, we have to assume the existence of an electrochemical potential gradient on the frontier. However, the unknown geometry of such an interface impedes the use of the classical theory for a planar one [5, 6].

Starting from a new theory named TEISI (Transfert d'Energie sur Interface à Similitude Interne) [7], developed in the Laboratoires de Marcoussis, in an attempt to understand the electrochemical transfer and transport in

porous media [8], the frontier of the segregated domains has been shown to be characterized by a "self similar" geometry [9]. The Hausdorff-Mandelbrot (H.M.) dimension of this geometry [9] is an integer or non-integer D value ($0 < D \leq 2$). It is given the name "fractal" [9].

It is characterized by scaling properties [9 - 11], *i.e.*,

- (a) image independence of optical magnification;
- (b) Hausdorff measure [12] higher than the topological one;
- (c) Richardson length [13], or electroactive interface, defined by $l = l_0^D \eta^{1-D}$ where l_0 is the apparent length of the interface, η is the elementary unit of the measure, and D is the H.M. dimension.

The H.M. dimension is defined as follows: If each unit of the interface is replaced by N (self) similar units having a scale coefficient given by $\alpha = l_0/\eta$, then, $\eta^D N = l_0^D$. l_0^D is a geometrical constant of the "fractal" named "contentant" (Fig. 1).

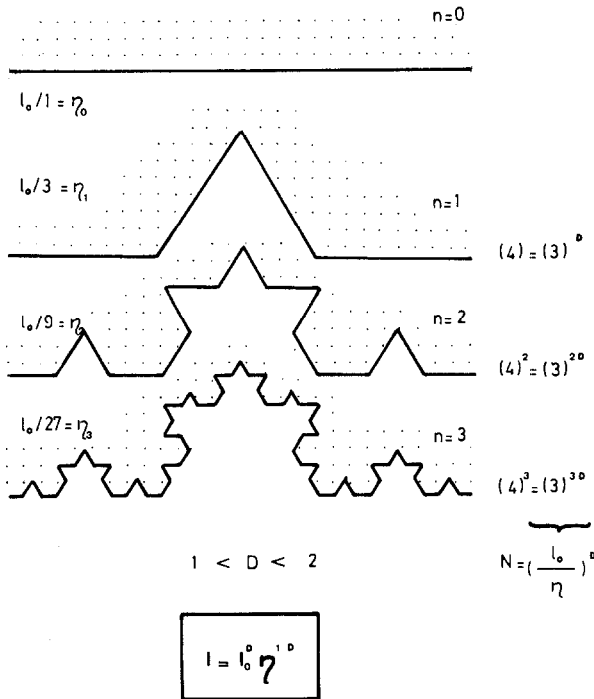


Fig. 1. Building of a self similar structure (Fractal), having a space dimension $D = 1.27$. l is the length of the Richardson interface. This curve may be the model of the rough surface.

$D = 1$ if the interface is a classical one; $D = 2$ means that the interface is a Peano curve [14] and the system is then controlled by the diffusion migration of the ion; $D \cong 1.5$ is a non-integer random fractal dimension [9]. D may be lower than 1 if the rich domain is clustered in the poor domain [7].

The "TEISI" model describes a first order transfer controlled by the phenomenological linear relation between the macroscopic exchange flows $\phi(t)$ and the local driving forces $A(t)$, through the Richardson interface: then

$$\phi(p) = k_o I_o^D \eta^{1-D}(p) A(p) \quad (1)$$

where k_o is a constant, and $p = i\omega$ is Laplace's variable.

Some assumptions about the storage of the species in the "fractal" geometry lead to the relation

$$\eta(p) = \eta_o / p^{1/\Delta} \quad p = i\omega \quad (2)$$

where η_o is a constant, $\Delta = D$ if the driving force is controlled by the transfer, $\Delta = 2D$ if the driving force is controlled by the diffusion in the "fractal", and $\Delta = DD'$ if some non-integer super scaling effects occur (a fractal of dimension D' in a fractal having a dimension D).

This major relation means that a space/time coupling occurs *via* the kinetics. Finally, the major result of this kinetic theory shows that the stationary macroscopic flow $\phi(t)$ *vs.* the local driving force $A(t)$ relation, through the D dimension self-similar interface (SSI), is given by:

$$\frac{d^n}{dt^n} \phi(t) = kA(t) \quad n = \frac{1}{\Delta} - 1$$

where k is a constant and d^n/dt^n is a non-integer differential operator [15]. According to irreversible thermodynamics [16], $\Delta = 1$ gives a fluxes/forces phenomenological relationship. According to Oldham's studies [17], $\Delta = 2$ agrees with the diffusion process. In this latter case, the Richardson interface is a Peano curve. The chemical diffusion process is therefore a most usual case of the TEISI model, but not the only one. This equation leads to three consequences which can be experimentally tested.

(1) All percussional relaxation processes follow the Curie-von Schweilder law, the most common being $t^{-1/\Delta}/\Gamma(1-1/\Delta)$ ($\Gamma(-n)$ being Euler's function), and leading to the D value which should be independent of the non-geometric parameters.

(2) First order transfer processes on a D fractal interface give a Cole and Cole FT transfer function [7]

$$FT\alpha \frac{1}{1 + (i\omega)^{1/\Delta}/k}$$

from which Δ values can be derived.

(3) Catastrophic kinetic changes at the transition time τ_i through constant macroscopic flow ϕ_i follow $\phi_i^\Delta \tau_i = \text{const.}$ [18].

This relation is named the "time-scaling" law. $\Delta = 1$ gives Faraday's law, $\Delta = 2$ is related to Sand-Karaoglanoff's law [5]; if $1 < \Delta < 2$, Δ is the Peukert coefficient [7, 18].

The great accuracy of this theory with the kinetics in porous media was recognized in 1980 [7]. In addition it has been pointed out that the electro-

chemical limitation in solid state insertion kinetics of the lithium ion through the lamellar Li_xFeS_2 structure is fittingly described by the TEISI model [15]. Indeed, as shown in Fig. 2 which gives the thermodynamic data, the phase diagram of the non-stoichiometric compound consists of two parts:

(a) $x \leq 1.09$: the structure is diphased and the frontier between lithium-rich and poor domains might be a random self similar one ($D_{\text{th}} = 1.5$);

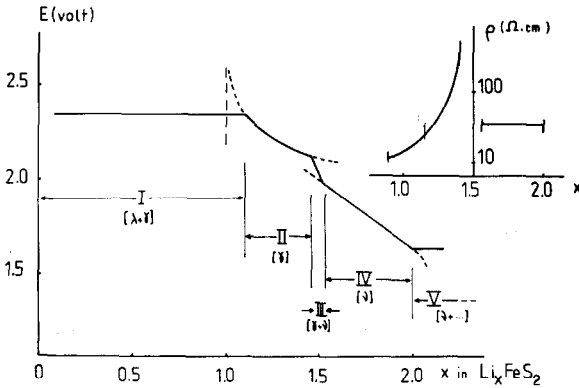


Fig. 2. Thermodynamic data for Li_xFeS_2 layered non-stoichiometric compound [1].

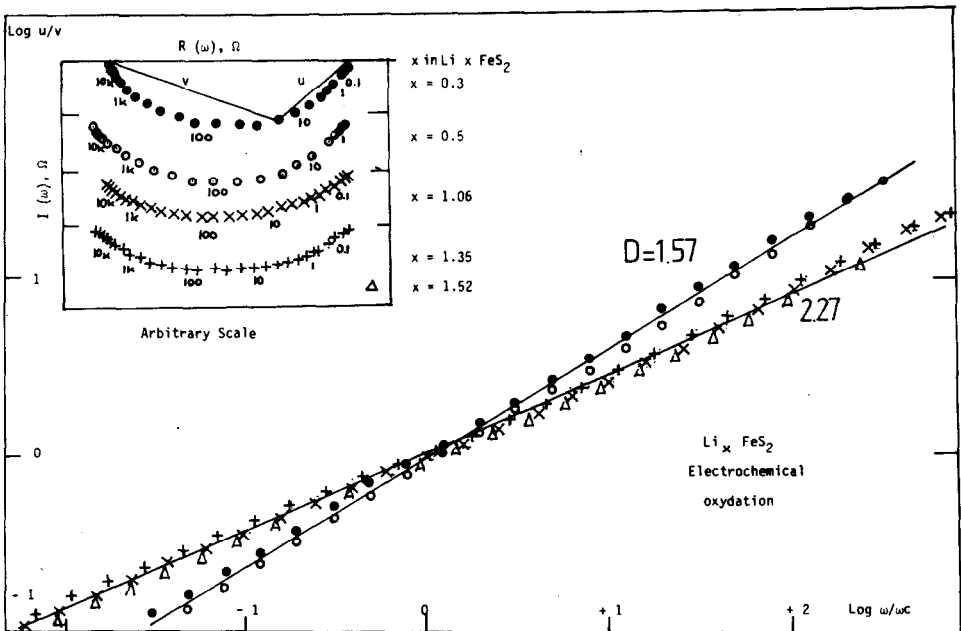


Fig. 3. Example of Faradaic impedances analysed from the major property of the Cole-Cole spectra: $(\omega/\omega_c) = [u(\omega)/v(\omega)]^D$. ω_c is the critical frequency, D is the H.M. dimension, $D = 2$ means that the Richardson interface is a Peano curve. Non-integer D means the existence of a fractal interface for the transfer.

(b) $x > 1.09$: Li_xFeS_2 is a single, non-stoichiometric phase ($D_{\text{th}} = 2$). D_{th} is the theoretical value for D .

These hypotheses are in fair agreement with the kinetic data:

(a) Faradaic impedances depend on frequencies like a Cole and Cole transfer function (Fig. 3). A Cole and Cole parameter gives fractal dimensions close to the theoretical values [$D(x \leq 1.09) \cong 1.6$; $D(x > 1.09) \cong 2.2$].

(b) The relaxation of the Dirac pulses presents a Curie-von Schweidler form, and the Hausdorff-Mandelbrot dimensions at equilibrium are close to the former one (Fig. 4).

The same tests in a steady state during the reduction show that the structure is two phased over all the non-stoichiometric domain ($x \leq 1.5$) and the kinetic limitation never agrees with the diffusion theory; Curie-von Schweidler's law as well as Peukert's law lead to a D value close to 1.5 ± 0.15 [18, 19].

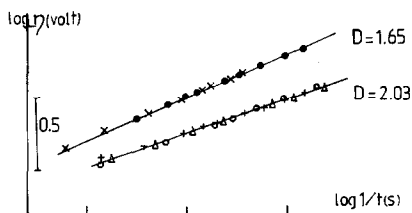


Fig. 4. Curie-von Schweidler type of relaxation. Values of x in Li_xFeS_2 : ●, 0.30; ×, 0.59; +, 0.84; ○, 1.36; and △, 1.50. $I(\text{mA}/\text{cm}^2) = 0$, $\Delta I = 6 \text{ mA}/\text{cm}^2$.

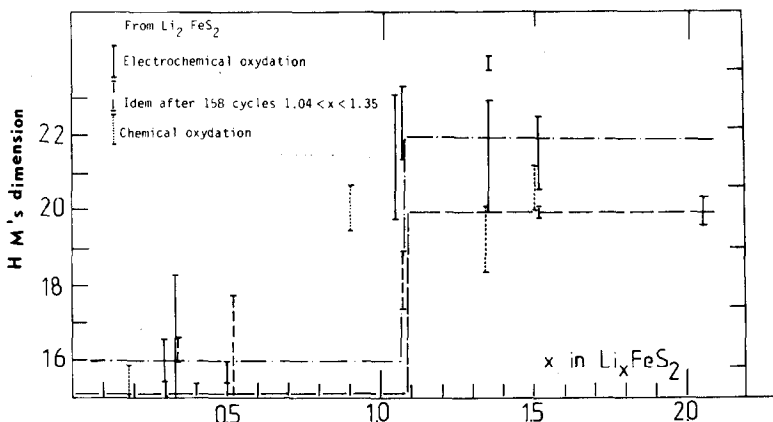


Fig. 5. Comprehensive view of the relation between the H.M. dimension, here given for different kinds of tests, and the reduction rate (x) of the layered, non-stoichiometric compounds Li_xFeS_2 . $D = 2$ means a diffusion control. $D < 2$ means a fractal control. — Expected values for single crystal ($D' = 1.0$). - - - Expected values for self-similar porosity with $D' = 1.1$.

Figure 5 shows the D value vs. x in Li_xFeS_2 . The small difference between the theoretical and observed values may be related to a chemical hyperscaling consequence [7] originating in the slight self-similar porosity of the monogranular electrode ($D' = 1.1$ — grain size $\cong 30 \mu\text{m}$ — electrode thickness $\cong 100 \mu\text{m}$).

Acknowledgments

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