

THE FRACTAL ANALYSIS OF BATTERY PERFORMANCES (EXTENDED ABSTRACT)*

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The discharge of an electrochemical cell can take place in several ways (*e.g.*, constant load, constant current, constant power). In this presentation attention will be focussed on constant current discharge.

The temptation to treat the galvanostatic response of an electrochemical system as a linear response to a current step, is strong. Nevertheless, an examination of standard discharge curves under constant current conditions (potential $E(t)$ versus time, t) renders such a proposal untenable; the discharge curves exhibit three distinct domains:

- an instantaneous potential drop.
- a smooth potential evolution (decreasing or sometimes increasing);
- a final, rapid potential drop.

The last potential drop is generally considered to be related closely to non-linear processes (crystallization, species depletion, etc.). It signals the end of the discharge.

Because of the non-linearity, no transfer function or permanent impedance can lead to the observed galvanostatic characteristics. In consequence, potential responses $E(t)$, to two different currents, $I(t)$, cannot be separated from each other in a simple way.

Computer modeling techniques can be used to supply manufacturers' requirements. Such techniques, based on numerical simulations, take into account the distribution of the pores and their sizes, the electrolyte and faradaic resistivities, the dynamics of the reactions, etc. However, some important invariants and correlations are not evident in the simulations. A detailed analysis of the accuracy of the numerical models shows some discrepancies between model and experiment.

An example of an experimental invariant is given by the well-known Peukert's law: capacity, $C = It_0$, is inversely proportional to the current I raised to a power n ; that is:

$$C(I, E_0) = Q(E_0)I^{-n} \quad (1)$$

t_0 is the battery discharge time and E_0 is the cut-off potential at time t_0 [1]. With $n = 0$, the battery behaves ideally according to the Faraday balance;

*The complete conference text and data are available from the authors on request; see also refs. 2, 4 and 5.

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with $n = 1$, eqn. (1), known as Sand's law, is characteristic of the diffusion-limited discharge on a planar interface. As shown previously [1] an MnO_2 alkaline electrode exhibits a value of $n = 0.38$, whereas in lead-acid batteries n is close to 0.4.

Moreover, it may be shown that Peukert's exponent n is reasonably independent of the cut off value, E_0 , provided that the discharge curves have been corrected for ohmic voltage drop. Furthermore, a particular constant current discharge curve (I_1) may be superposed on another curve at a constant current (I_2) by a transformation of the time axis in the ratio $(I_1/I_2)^n$, together with a translation along the E axis to take the instantaneous potential drop into account. The discharge curves thus preserve finiteness with respect to the time.

By using a particular curve as a reference, one may take account of the complexity of a reaction without any knowledge of it. Chemical kinetics may even be totally disregarded.

In addition it can be shown that n does not depend on the chemistry of the reaction or on the physico-chemical limitations of the discharge. If the batteries or their electrodes are well thermostatted, these properties are general and may be checked by various electrochemical systems (either

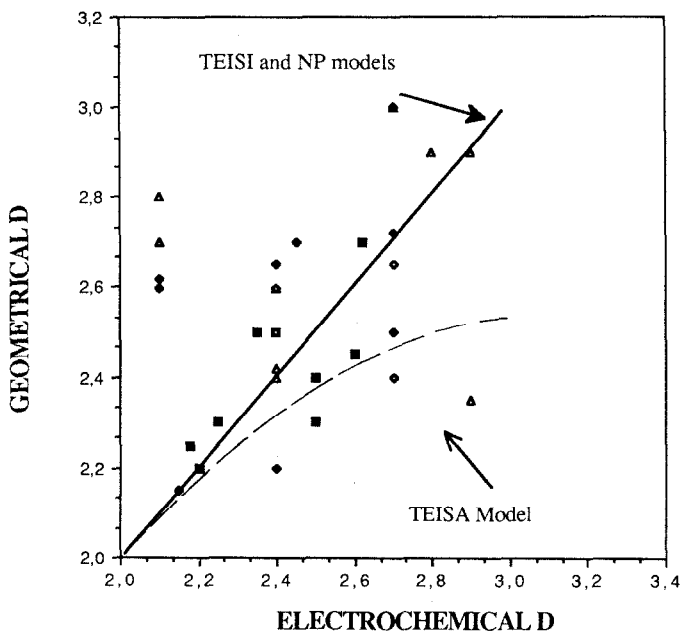


Fig. 1. Correlation between fractal dimension measured by X-ray scattering [Y] vs. fractal dimension obtained through electrochemical measurements [X]. X-ray scattering on dry and wet carbons. Electrochemical results from Fractance analysis [Constant Phase Angle dispersion] (\bullet , \square , \triangle) and from Peukert's law (\blacksquare). Characteristic frequencies for fractance analysis $1 \cdot 10^{-4}$ Hz.

macro or micro, organic or mineral, solid or liquid ...). The experimental conclusion is that the origin of Peukert's law and of the time affinity would be found in a geometrical invariant. This law may be explained within the framework of the TEISI [2], N.P. [3] models or within the TEISA model [4, 5].

It will be shown in the presentation that the Peukert coefficient n and the fractal dimensions are related either to the frequency dispersion of any reaction occurring on the porous electrode, and equally to the energy balance in the medium (Electrochemical D), or to the scaling law of the X-ray scattering on the electrode [geometrical D (Fig. 1)].

The model will be developed to include the diffusion in fractal media and used to emphasise the importance of the movement of the electroactive species on the interface.

References

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