

Transient techniques and electrochemical reactions in solid state

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Transient techniques are used to obtain a clear view of the reaction mechanisms. They are specially well adapted to the study of electrochemical system since the energy level and reaction rate can be easily followed and recorded. A large body of literature has been devoted to the analysis of transient responses in liquid electrolytes. The aim of the present talk is to extend the use of transient electrochemical techniques to the study of reactions in solid state. Three typical research fields were investigated:

- metal deposition and alloys formation
- metal deposition and electrode coating
- intercalation compounds and phase transition processes (lithium batteries).

A special attention was devoted to the specific features of these systems which have not yet been included in the classical treatment of pulse techniques, i. e. *i*) the movement of the solid electrode boundary motion during the metal incorporation, *ii*) the change in the electroactive area due to nucleation and crystal growth, *iii*) the influence of the departure to ideality (gradient of chemical potential), *iiii*) the concentration and distance dependence of the diffusion coefficient, D .

Some effort has been done to solve the theoretical equations taking into account these phenomena. Algebraic solutions were found in some cases, such as the influence of boundary motion or concentration dependence of D in chronoamperometry or chronopotentiometry. Unexpectedly, it is shown that these factors do not affect the shape of the transient response, which seems to obey the classical Sand or Cottrell's laws. This behavior may lead to erroneous results since the proportionality coefficient in the equations is strongly affected by the perturbing factors. In most cases, it was not possible to obtain a mathematical analysis of the transient response. Digital simulation was the only way to treat the phenomena comprehensively. It consists in solving the partial differential equations of transport by numerical calculation taking into account the boundary conditions coming from the experimental constraints.¹

The technique was used to analyse by cyclic voltammetry the quality of the metal coating in electrodeposition, the shape of the stripping peak depends strongly on the size of the first metallic crystals (Fig. 1). These programs were used to solve the problem of charge-discharge cycles of lithium batteries,² and to take into account the concentration dependence of the diffusion coefficient and of the thermodynamic enhancement factor (Fig. 2). They prove to be useful in studying the behavior of phase transition phenomena which often occur during the intercalation processes (Fig. 3).

1. F. Lantelme, Modelling and Simulation in Fused Electrochemistry of Metals, in *Metallurgical and Engineering Materials Science*, Metallurgical Industry Press, p. 133, 1996, Beijing.

2. F. Lantelme, A. Mantoux, H. Groult and D. Lincot, *Electrochim. Acta*, 47 (2002) 3927.

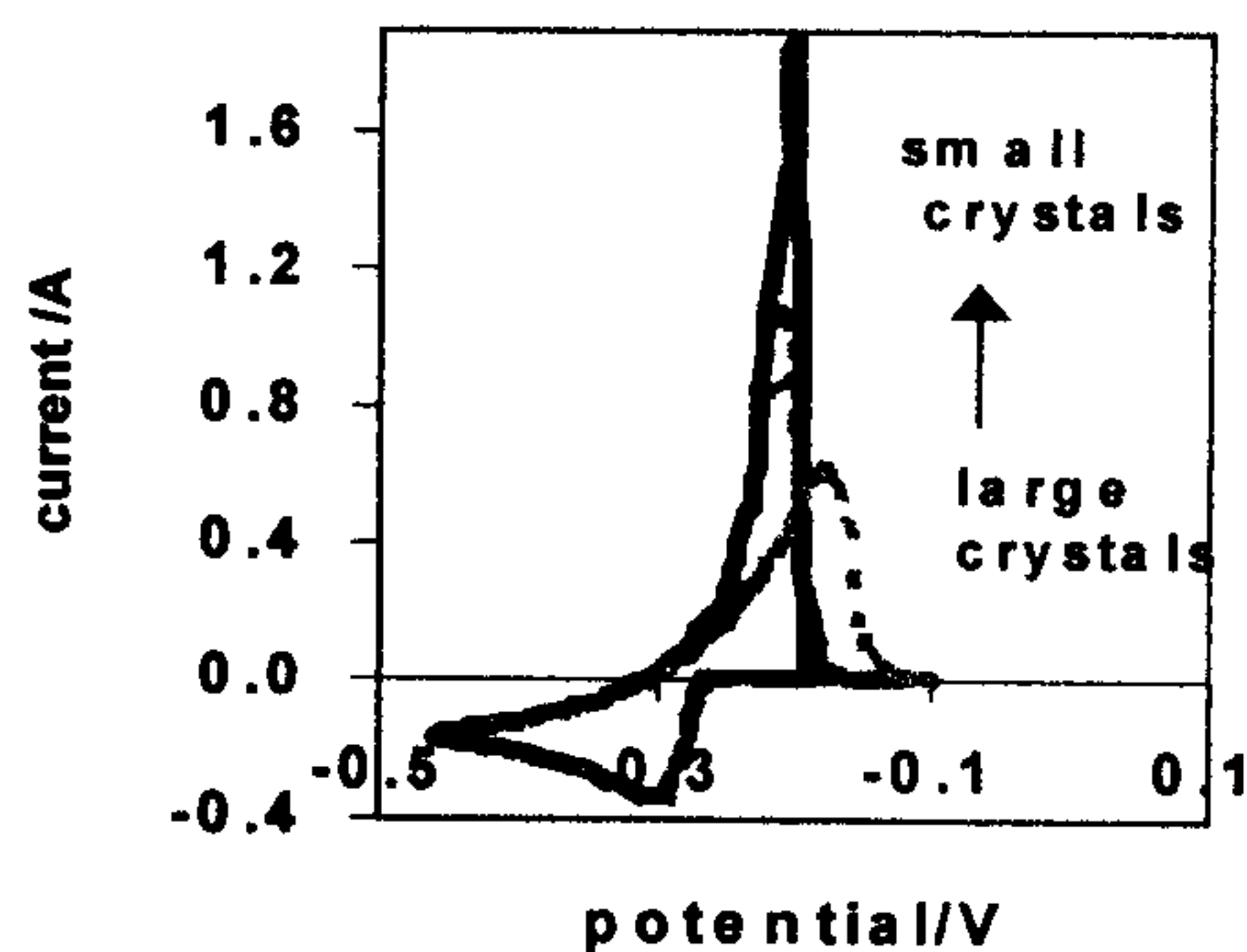


Fig. 1. Cyclic voltammogram for electrodeposition of metal.

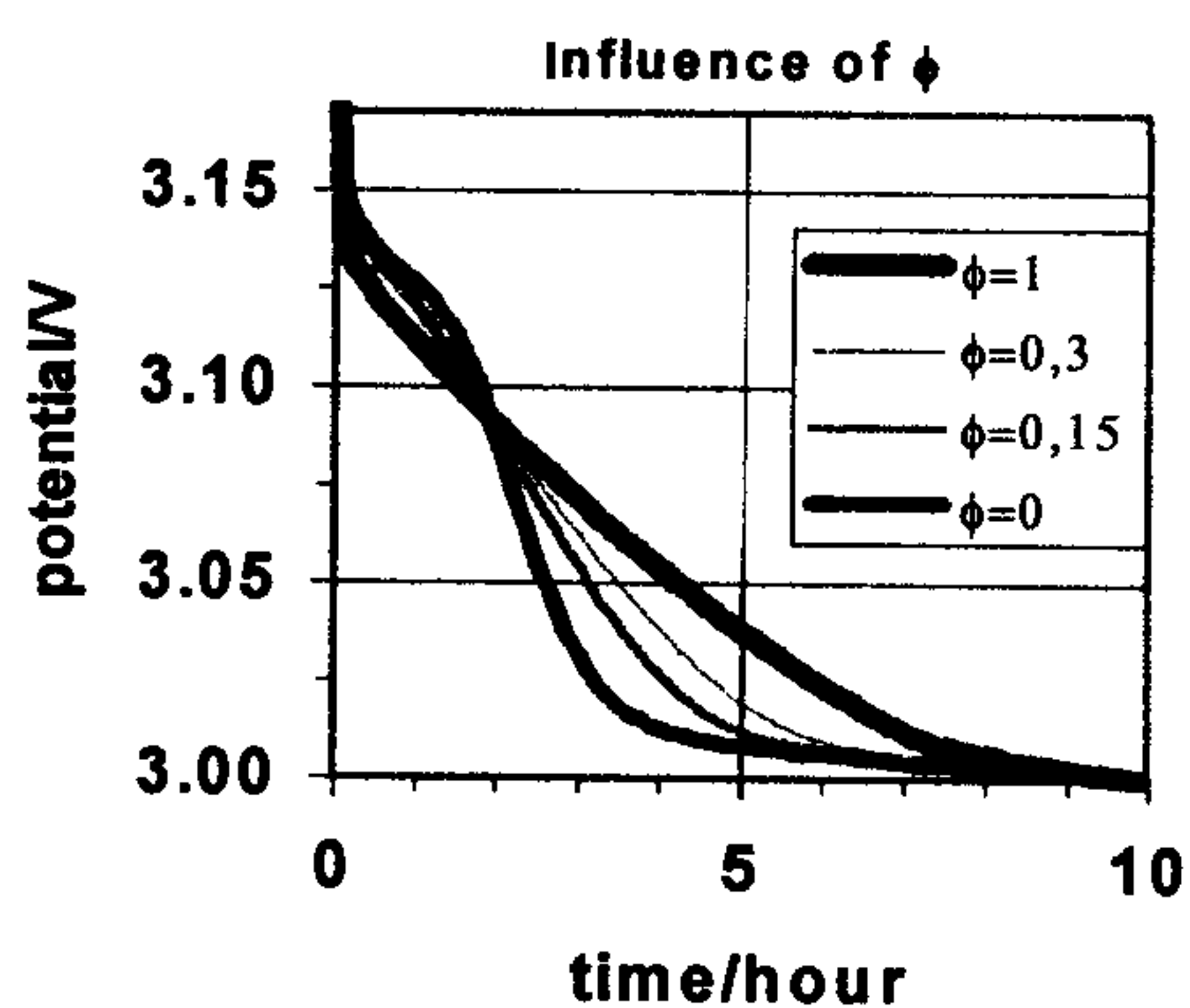


Fig. 2. Influence of the thermodynamic enhancement factor on the shape of chronopotentiogram during metal incorporation with a phase transition process (ϕ , proportionality coefficient, $\phi=0$, no influence; $\phi=1$, full influence).

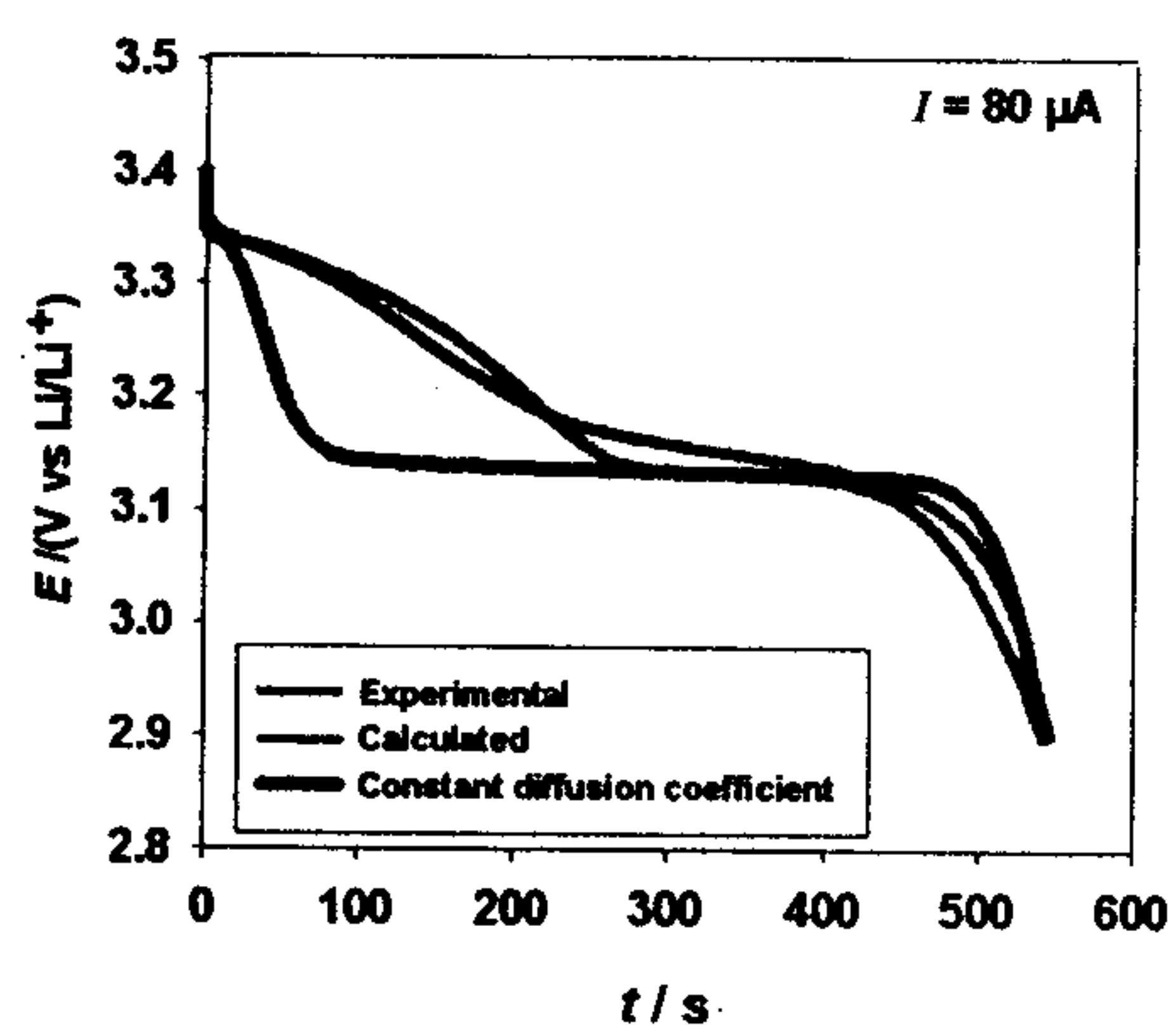


Fig. 3. Chronopotentiograms for lithium insertion into a V_2O_5 thin film. Experimental and calculated curves for a fixed or variable diffusion coefficient.