

Techniques for the Study of Electrode Processes

Ernest Yeager and Frank Ludwig

Department of Chemistry
Western Reserve University and Case Institute of Technology
Cleveland, Ohio

The electrochemist is faced with two types of problems in undertaking an experimental study of the kinetics of a particular electrode system.

1. Identification of all of the factors or parameters which must be known and controlled in order to carry out interpretable experiments.
2. Choice of the most promising instrumental techniques for the study.

In conjunction with the first, it can not be emphasized too strongly that the real pitfall in electrochemistry is not the lack of sophisticated instrumental techniques and methods but rather that these techniques do not give adequate knowledge or control over many of the physical and chemical variables which have a major effect on electrode processes. The choice of techniques to be used to study the kinetics of a particular electrode process requires a projection as to the probable mechanism and the magnitude of the corresponding rate constants, the extent of mass transport control and ohmic losses, and then a best matching up of the requirements imposed by these factors to the available techniques. Only then can the experiment be properly designed.

This paper will attempt to identify the critical experimental parameters that must be controlled in electrode kinetic studies and indicate approaches to their control. The various steady-state and transient techniques available for establishing kinetic parameters will then be compared. Some of the features of these methods are summarized in Table 1. Important experimental problems and factors which need to be controlled in electrode kinetic studies are listed in Table 2 together with the procedures or techniques most promising for affecting their control.

Both steady-state and transient techniques have found extensive use in kinetic studies of electrode processes. The most common means for perturbing electrode systems from equilibrium involve the application of some well-defined current or voltage function but such techniques are difficult to apply to electrode systems of high resistivity in the solution or electrode phase (*e.g.*, oxides, organic semiconductors). In such instances changes in temperature, pressure, concentration, or surface area may be used to perturb the electrode system with the relaxation followed by the measurement of the electrode potential--thus avoiding the passage of any appreciable current through the system (see Table 1).

Acknowledgment

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Table 1. Typical electrical methods for the study of electrode kinetics.

Technique	i-E-time controlled variable	dependent variable	Maximum k_s (cm/sec)	Remarks
<u>Steady State</u>				
1. direct potentiostatic	E	i	10^{-2}	Instrumentation simple. Progressive changes in electrode surface cause serious problems in many instances. Can be carried out with very slow voltage sweep (sufficiently slow for capacitive current to be negligible).
2. direct galvanostatic	i	E	10^{-2}	Instrumentation very simple. Progressive changes in electrode surface cause serious problems in many instances. Can be carried out with ramp function of low slope. Not recommended for systems involving limiting currents or maxima in i vs. E curves.
3. indirect galvanostatic (interruption)	i	E	10^{-2}	Yields steady state polarization but also can be used to obtain E vs. t information after interruption of current. Virtually eliminates IR correction problem without use of Luggin capillary. (Other remarks same as for direct galvanostatic method.)
<u>Non-Steady State</u>				
1. voltage step	E	i	100	IR drop between working and reference electrodes must be very small. Requires correction at short times for double layer charging. Requires fast action potentiostat plus oscilloscope.
2. cyclic linear sweep voltammetry-slow sweep (< 1 V/sec)	E	i	10^{-2}	Complete analysis very complex. Effective technique for preliminary studies to identify various features. If dE/dt is sufficiently small, may be equivalent to steady state. IR drop between working and reference electrodes must be very small. Requires potentiostat and fast recorder or oscilloscope.

Table 1. Typical electrical methods (continued)

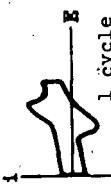
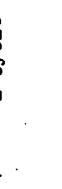
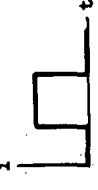
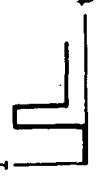
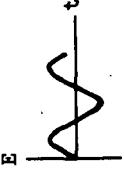
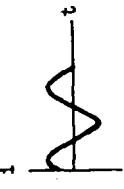
Techniques	controlled variable	i-E-time dependent variable	Maximum k_s (cm/sec)	Remarks
3. cyclic linear sweep voltammetry-fast sweep (>1 V/sec)			10^{-1}	Complete theoretical analysis very complex. Yields information concerning adsorption kinetics (particularly fast). Effective technique for preliminary examination of surface. IR drop between working and reference electrodes must be very small. Requires fast action potentiostat plus oscilloscope.
4. single current step			10^0	Instrumentation relatively simple (pulsed galvanostat plus oscilloscope). Relatively easy to correct for IR drop. Requires correction for double layer charging.
5. double current step			10^1	Adjust height-width of first current pulse such that $(dE/dt) = 0$ at beginning of second current pulse. Avoids double layer charging correction. Requires more complex instrumentation than single current step method (double current pulse Generator plus oscilloscope). Relatively easy to correct for IR drop. For very fast kinetics, must consider diffuse layer-diffusion layer interactions.
6. a-c impedance at reversible potential			10^1	Requires measurements over a range of frequencies to separate double layer and kinetic effects. High accuracy possible. Transfer coefficient not determined directly; evaluate from dependence of i_0 on concentration. Keep a-c voltage low to avoid non-linear effects. Requires a-c bridge or a-c generator plus oscilloscope.

Table 1. Typical electrical methods (continued)

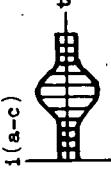
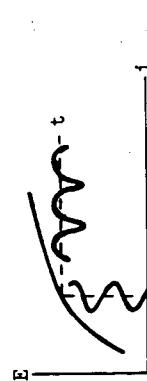
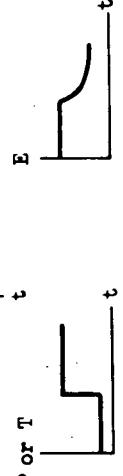
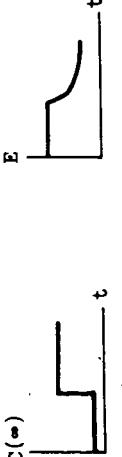
Techniques	controlled variable	i-E-time dependent variable	Maximum k_s (cm/sec)	Remarks
7. a-c impedance with d-c potential ramp	E		10^1	Theoretical analysis complex. Can yield information concerning adsorption changes in double layer. Instrumentation rather complex (fast action potentiostat with a-c and ramp function generators plus phase meter, detector, and recorder or oscilloscope).
8. Faradaic rectification and distortion	E		10^2	For very fast processes. Requires sophisticated equipment for very fast processes (rated r-f current source capable of providing power). Heat effects can be a problem. Diffuse layer-diffusion layer interactions must be considered for very fast kinetics.
9. Pressure or temperature step techniques	P or T		10^1 (P step)	After disturbance, relaxation is similar to that with electrical perturbation techniques. Offers advantage that fast kinetics can be studied in systems with insufficient conductivity to pass appreciable current. Pressure step easily obtained with bursting diaphragm (10^{-5} sec resolution).
10. Concentration perturbation method	C(∞)		10^{-1}	After disturbance, relaxation is similar to that with electrical perturbation techniques. Offers advantage that high resistivity can be tolerated. Flow techniques provide convenient means for producing change in bulk concentration (10^{-3} sec resolution).

Table 2. Typical experimental problems and factors to be controlled in the study of electrode processes in aqueous systems.

Problem or factor	Techniques for controlling or measuring	Remarks
1. Impurity effects		
a. solution purity	<ol style="list-style-type: none"> 1. Use the best of conventional physical and chemical purification procedures (multiple stage distillation, recrystallization, chromatographic purification) followed by <u>in situ</u> adsorption-pre-electrolysis with forced convection at various controlled potentials. Continue adsorption-pre-electrolysis until no further change in kinetics evident. 2. Use a minimum volume of solution for a given area of electrodes. 	Probably adequately controlled only in most careful work. Impurities can cause difficulty at small fractions of monolayer coverage if critical sites are blocked or if electronic properties of surface are disturbed in a non-localized manner (e.g., d-orbital poisons). [Monolayer corresponds to 10^{-9} moles/cm ² of true electrode area.] Beware of introducing impurities into solution (e.g., platinum) through pre-electrolysis.
b. electrode phase	<ol style="list-style-type: none"> 1. Use easily purified metals whenever possible (but life is not this simple!), e.g., mercury. 2. Start with highest purity electrode materials available. 3. Where practical, use zone refining, distillation, etc. 	Electrochemists often use metals with low concentrations of spectrographically detectable elements. These metals are often contaminated very substantially with other elements for which emission spectroscopy is not sensitive. Recommend checking impurities with mass spectrometer.
c. gases used to saturation solution and above solution	<ol style="list-style-type: none"> 1. H₂ readily ultrapurified with Pd diffuser. 2. He readily purified with molecular sieve-diffuser or liquid N₂-adsorbate trap. 	Gases other than H ₂ and He more difficult to purify. When possible, use these. Beware of Teflon or other plastic tubing for connections to cell--O ₂ permeable.
d. cell construction materials	<ol style="list-style-type: none"> 1. Use high purity glass (low As particularly for H-overpotential) for acid and neutral media; fabricate glass cell with H₂ flame; do not blow directly with breath; treat with solution for prolonged period to leach out dissolvable impurities. 2. Use Teflon for alkaline, acid, or neutral media; use great care to minimize contamination in machining; use oxidizing solution to remove organic contaminants; treat with solution for prolonged period. 	Glass is unsatisfactory for alkaline solutions. Teflon is porous and soaks up solution components--difficult to remove; also permeable to O ₂ .

Table 2. Typical experimental problems and factors (continued)

Problem or factor	Techinques for controlling or measuring	Remarks
e. atmospheric pollution	<ol style="list-style-type: none"> 1. Use high vacuum techniques. 2. Where such techniques are unpractical, use controlled atmosphere enclosure with non-contaminating atmospheres. 3. Carefully out-gas all solutions to remove last traces of oxygen. 	Small traces of oxygen difficult to keep out of system and to remove from solutions.
f. contamination from counter and reference electrodes	<ol style="list-style-type: none"> 1. Choose counter and reference electrode so as to be compatible with system or place in well isolated compartments. 	Pd diffuser hydrogen electrode often attractive for high current density counter electrode.
2. Non-uniform current distribution and non-uniform surface concentrations of reactants and products	<ol style="list-style-type: none"> 1. Use spherical electrodes or guard electrode arrangement (e.g., ring-disc assembly). 2. Maximize the ratio of differential reaction impedance to solution resistivity. 	Kinetic studies require uniform current distribution. Avoid closely placed Luggin capillary. Beware of porous electrodes.
a. resulting principally from potential gradients in solution	<ol style="list-style-type: none"> 1. Redesign electrode. 	Unlikely in properly designed electrodes for kinetic studies. Often encountered in applied electrochemistry.
b. resulting principally from potential gradients in electrode	<ol style="list-style-type: none"> 1. Use electroconfigurations giving uniform Nernst diffusion layer thickness (e.g., rotating disc or ring-disc assembly). 2. Use sufficient convection that concentrations at surface are essentially the same as in bulk solution even though Nernst diffusion layer is non-uniform in thickness. 3. Avoid convective transfer through use of transient techniques. 	Avoid use of closely placed Luggin capillary.
c. non-uniform mass transport along electrode resulting from differences in boundary layer thickness	<ol style="list-style-type: none"> 1. Use electroconfigurations giving uniform Nernst diffusion layer thickness (e.g., rotating disc or ring-disc assembly). 2. Increase conductivity through use of supporting electrolyte. 3. Use interrupter or similar step function technique to measure overpotential. 	More of a problem in potentiostatic control.
3. Ohmic drops included in measurements	<ol style="list-style-type: none"> a. within electrolyte 	

Table 2. Typical experimental problems and factors (continued)

Problem or factor	Techniques for controlling or measuring	Remarks
b. within electrode	<ol style="list-style-type: none"> 1. Redesign electrode to minimize-if possible. 2. Use interrupter or other step function technique to measure. 	A problem in studies with semiconductor electrodes (<u>e.g.</u> , oxide, organic semiconductors, etc.).
4. Mass transport control predominant; insensitivity to kinetics	<ol style="list-style-type: none"> 1. Use more effective convection (<u>e.g.</u>, high speed rotating electrode, ultrasonics). 2. Use non-steady state technique better suited to study of fast kinetics (<u>e.g.</u>, stepfunction technique, Faradaic rectification, etc.). 	See "Table 1 for range of formal rate constants accessible with various techniques.
5. Topographical features of solid electrodes	<ol style="list-style-type: none"> 1. Use step function or sweep methods which permit completion of measurements before substantial changes in surface structure have occurred. 2. Use great care in mechanical and chemical polishing and annealing. 	A major problem in studies of deposition and dissolution. A major reason for favoring liquid metals for kinetic studies. Single crystals may help somewhat in some instances but do not eliminate problem.
a. time variance and reproducibility problems (area, micro-crystallographic orientation of surface, defect concentration, etc.)	<ol style="list-style-type: none"> 1. Capacity measurements at a given potential provide indication of relative values for true area. 2. Gas adsorption measurements (BET), other adsorption techniques. 	Microcracks, porosity, etc., can cause serious complications. Try to avoid kinetic studies on porous electrodes.
b. determination of: true area	<ol style="list-style-type: none"> 1. Etch pit studies combined with electron and ordinary optical microscopy and LEED. 	Applicable only to systems with relatively high true/apparent area ratio.
micro orientation of the surface, defect concentration	<ol style="list-style-type: none"> 1. Etch pit studies coupled with electron and optical microscopy. 	Requires experience and facilities which most electrochemical kineticians do not have.
surface defect concentration	<ol style="list-style-type: none"> 1. Etch pit studies coupled with electron and optical microscopy. 	Much room for improved techniques.
6. Electrical double layer a. potential drop across diffuse ionic layer and concentration of species in pre-reaction layer (not specifically adsorbed)	<ol style="list-style-type: none"> 1. Determine point of zero charge (pzc) from interfacial tension, differential capacity, and/or other methods (hardness, ATR, etc.) and then calculate potential drop across diffuse layer and concentrations in Helmholtz plane from these data. Works well with Hg, more complicated with solid electrodes, particularly with adsorbed hydrogen or oxygen. 	On some limited occasions (particularly at potentials remote to the pzc with concentrated supporting electrolyte), the potential drop across diffuse layer can be assumed approx. constant and the concentration of reacting species in the Helmholtz plane proportional approx. to bulk concentration provided no specific adsorption.

Table 2. Typical experimental problems and factors (continued)

Problem or factor	Techniques for controlling or measuring	Remarks
b. concentration of specifically adsorbed species--both reactants and non-reactants	<ol style="list-style-type: none"> 1. Measure directly by <u>in situ</u> optical or radiochemical method. 2. Determine from voltammetry, charging curves, impedance measurements. 3. Determine from interfacial tension--capacity measurements--Gibbs adsorption eq. 	A necessity in virtually all kinetic studies.
c. potential drop across and carrier concentration in space charge layer in semiconducting electrode	<ol style="list-style-type: none"> 1. Attempt to calculate from capacity measurements and kinetic behavior of redox couples on surface. 	With higher carrier concentration, potential drop across space charge layer may be negligible and carrier concentration proportional to bulk concentration. With low carrier concentrations, potential drop across space charge layer may be much larger than drop across interface and changes in carrier concentration at surface of semiconductor may be the predominant factor responsible for the dependence of the current on electrode potential. Space charge layer and nonlinear characteristics of metal-semiconductor interface can cause serious complications in interpreting double layer and kinetic studies at semiconductor-electrolyte interfaces.
7. Competing electrode reactions	<ol style="list-style-type: none"> 1. Evaluate rates by various analytical methods. 	Can cause pH and other changes which must be considered in addition to fact that overall current corresponds to more than one process.
b. suppression	<ol style="list-style-type: none"> 1. When possible, use electrodes and solutions not conducive to the particular competing process (high hydrogen overpotential metals, inert metals, etc.). 	Often not possible.
8. Reaction intermediates	<ol style="list-style-type: none"> a. identification 	<ol style="list-style-type: none"> 1. Use analytical technique to identify in bulk. If very unstable or transient, try ATR, ESR, voltammetry on ring with rotating ring-disc technique, etc.
		Very difficult if only present as adsorbed species.

Table 2. Typical experimental problems and factors (continued)

Problem or factor	Techniques for controlling or measuring	Remarks
8. Reaction intermediates (continued) b. measure concentra- tion	Use rotating ring-disc techniques, double pulse or chronopotentiometry with current reversal techniques, ATR, etc.	Rotating ring-disc technique particularly useful.