

## A Simple and Unique Method for Achieving Open Circuit Conditions during Spectroelectrochemical Measurements

ELISABET AHLBERG, JAN HALVORSEN and VERNON D. PARKER \*

Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Open circuit relaxation experiments are useful in studying the kinetics and mechanisms of the reactions of electrode generated intermediates. The potential of the test electrode is stepped from a region where no current flows to a value where the charge transfer of interest occurs at a diffusion controlled rate. After a given period of time, the test electrode is disconnected from the potentiostat and the decay of the electrode generated intermediate brought about by a homogeneous chemical reaction is monitored spectrally.<sup>1,2</sup> Disconnection of the test electrode is normally achieved by electronic switching and the time necessary for the discharge of the electrical double layer, estimated to be of the order of 100  $\mu$ s,<sup>2</sup> is the limiting factor for relaxation studies. Here we report a method that allows the open circuit condition to be realized very rapidly without employing a switching circuit.

Semiconductor diodes have the property of low resistance to the flow of current in one direction while having very high resistance in the opposite direction. Two identical diodes connected in parallel but with opposite polarity provide an equal resistance to the flow of current in both directions. When the diodes are connected between the working electrode and virtual ground of the current follower, the apparent potential in the forward and backward scans during cyclic voltammetry is equal to  $E + IR$  and  $E - IR$ , respectively, where  $E$  is the electrode potential,  $I$  the current and  $R$  the resistance of the identical diodes. Thus, the apparent potential separation for a reversible redox couple during cyclic voltammetry differs from the theoretical value by  $(I_A^P + I_C^P)R$  where the currents refer to anodic and cathodic peaks, respectively. The effect is illustrated by the cyclic voltammograms for the reduction of perylene to the stable anion radical in *N,N*-dimethylformamide containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) shown in Fig. 1. Direct connection of the potentiostat to the cell during cyclic voltammetry with a voltage scan rate of 100  $\text{mV s}^{-1}$  resulted in a typical voltammogram for a reversible one electron transfer with a potential separation of about 60 mV

for the oxidation and reduction peaks (Fig. 1a). When the diode circuit was connected, the cyclic voltammogram appeared as in Fig. 1b. Upon changing the direction of voltage sweep after the initial reduction peak R the current dropped to zero until the applied voltage reached a value positive enough to bring about the oxidation of the anion radical at peak O. The overall result is that R was shifted about 300 mV more negative and O about 300 mV more positive than the corresponding peaks of the voltammogram recorded without the diode connection (Fig. 1a). The magnitude of the potential shift is proportional to the current and hence to both the voltage sweep rate and the area of the electrode. The feature of importance is that the diode circuitry effectively creates a "dead" potential region where no current flows through the cell and this region fulfills the requirements for open circuit relaxation experiments.

We have observed that after open circuit, whether the condition is achieved by switching or by the diode "dead" region, generation of the intermediate continues for several hundred  $\mu$ s. The reaction that continues at the electrode surface after disconnection is that which results in the discharging of the electrical double layer. This phenomenon severely limits the use of spectroelectrochemistry for relaxa-

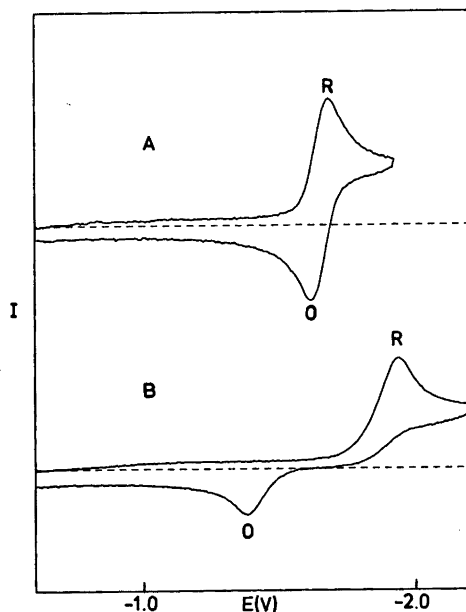


Fig. 1. Cyclic voltammogram for the reduction of perylene (1.0 mM) in dimethylformamide containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M). Normal connection (A) and with the diode circuit connected (B). Voltage sweep rate = 100  $\text{mV s}^{-1}$ .

\* To whom correspondence should be addressed.

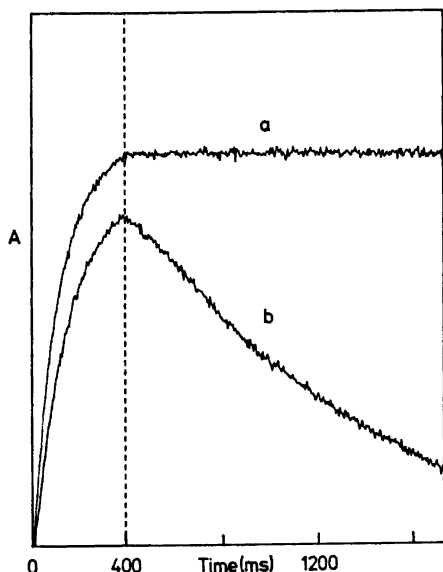


Fig. 2. Absorbance time curves for the spectroelectrochemical generation of perylene anion radical at 570 nm in dimethylformamide (a) and with the addition of phenol (b). The time to open circuit (dashed line) is 400 ms.

tion studies and we find that measurements cannot begin much sooner than 1 ms after disconnection. However, the applied potential waveform that we use for double step chronoamperometry<sup>3</sup> which resembles the "charge injection" technique used by Winograd<sup>4</sup> for single step experiments eliminates the problem. An initial 20  $\mu$ s pulse to about 2.5 V beyond the peak potential of the electrode reaction provides a rapid charging of the double layer after which the potential is dropped to about 200 mV above the peak potential in order to generate the intermediate. In order to achieve open circuit and rapidly discharge the double layer, a 20  $\mu$ s pulse of the same magnitude but opposite in polarity to the first is applied with the potential ending in the "dead" region where no current flows.

Application of the technique is illustrated for the reduction of perylene in DMF. Fig. 2a shows the absorbance time curve for the generation of perylene anion radical in the absence of proton donors. The dashed vertical line coincides with the open circuit condition. After open circuit, the absorbance time curve is flat showing that perylene anion radical is neither produced nor consumed. To illustrate the technique under kinetic conditions, the experiment was repeated after the addition of phenol (0.1 M). The absorbance-time curve in this case shows the characteristic exponential decay

after open circuit (Fig. 2b) due to the reaction between perylene anion radical and the proton donor. Analysis of the curve resulted in a pseudo first order rate constant equal to  $0.475 \text{ s}^{-1}$  under the conditions of the experiment.

Using the methods described here it is possible to apply open circuit relaxation during spectroelectrochemical experiments at much shorter times than when a simple switching procedure is used. This enables one to follow the rates of much more rapid reactions. Further work is in progress to attempt to measure the rates of very rapid reactions using this technique in conjunction with the new spectroelectrochemical cells which we have recently described.<sup>5</sup>

*Acknowledgement.* We gratefully acknowledge support for E. A. from the Norwegian Research Council for Science and the Humanities.

1. Blount, H. N., Winograd, N. and Kuwana, T. *J. Phys. Chem.* 74 (1970) 3231.
2. Kuwana, T. and Winograd, N. In Bard, A. J., Ed., *Electroanalytical Chemistry*, Dekker, New York 1974, Vol. 7.
3. Ahlberg, E. and Parker, V. D. *Unpublished work.*
4. Davis, J. E. and Winograd, N. *Anal. Chem.* 44 (1972) 2152.
5. Ahlberg, E., Parker, D. P. and Parker, V. D. *Acta Chem. Scand. B* 33 (1979) 760.

Received June 27, 1979.