

SHORT COMMUNICATION

ANOMALOUS OBSERVATIONS IN d.c.-POLARIZED TRANSIENT CONDUCTIVITY MEASUREMENTS IN AQUEOUS SOLUTIONS DUE TO ELECTRODE SURFACE EFFECTS

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Abstract—Transient conductance changes in aqueous solutions following a short pulse of radiation are almost universally performed using conductivity cells where chemically inert electrodes are in contact with the solution. The changes which are measured are usually small compared to the background conductance arising from the polar nature of the solvent and the presence of ionic solutes. This large background current may cause field distortions near the surfaces of the electrodes. These distortions may cause the resultant transient measurements to be incorrect, reflecting neither the magnitude nor the kinetics of the unperturbed radiation-induced conductance changes. The cause of these errors is discussed and representative observations are presented. A simple method of minimising and eliminating such errors is presented with the aim of improving the reliability and calibration accuracy of pulse-radiolysis conductivity installations.

The measurement of transient-conductance changes in solutions is a commonly used technique in pulse-radiolysis studies (Asmus, 1972; Asmus and Janata, 1981; Janata, 1982; Schmidt, 1972; Vojnovic *et al.*, 1986). Detection systems use either a.c. or d.c. excitation of the cell which usually consists of platinum electrodes in contact with the solution. The implicit assumption in all low-field transient conductivity measurements is that the drift velocity of the induced charges is much smaller than their average thermal velocity. A negligible proportion of radiation-induced charges is thus collected at the electrodes. In general, the time resolution of a.c. systems is limited to several cycles of the applied waveform; frequencies of tens of Hz to tens of MHz are used and since the field is reversed periodically, polarization effects are avoided. In the case of d.c.-excited systems, where the polarization voltage is applied in the form of a pulse only during the recording period, faster time resolutions can be achieved (Janata, 1982; Vojnovic, 1983; Vojnovic *et al.*, 1986). Such systems have been used even with solutions where the background conductance was large and have been reported to be suitable for use over a pH range of 3–11 or greater. In these cases, it is useful to examine the current flow during the applied polarizing voltage pulse as polarization and electrolysis can occur much more readily. More importantly, as is shown in some examples below, the transient current in the cell circuit may not reflect

accurately excess charge carrier changes induced by the radiation pulse.

Any current passing from one electrode to an electrolyte causes a chemical reaction and this current may thus produce changes in the chemical composition of the solution. More importantly in the case of transient measurements, concentration gradients may be set up between the electrodes which in turn may cause sometimes significant measurement errors. The passage of the current through the solution not only produces real variations in the conductance of the solution, but also sets up potentials at the electrodes which may invalidate both background and transient conductance measurements. The term polarization is used, often rather indiscriminately, to denote not only the concentration changes but also the changes in potentials at the electrodes resulting from these changes. Suitable precautions, in the case of steady-state measurement, to reduce polarization effects, which become more significant as the solution conductance increases, have been used for a century resulting in the "Kohlrausch method" of conductivity measurement. However, in the case of transient observations, measurement errors do not seem to have been examined in detail.

The kinetics of the current flowing in the cell due to an applied voltage step function can be divided into three regions. During and shortly after the rise of the voltage step, a large displacement current

flows, determined by the cell constant, i.e. the cell capacitance. Following this cell charging period, t_c , typically < 50 ns, the current will be determined by the solution conductance (G_c) and is then found to decay over a period of several milliseconds or longer, t_d , as the solution and electrodes polarize, to a value which is much lower and relatively constant (t_p). Eventually, electrolysis occurs and gas bubbles are formed at the electrodes.

The period t_d and the plateau level reached are influenced to a large extent by the state of the electrode surface, but the consequences of this have not been reported in the past. In previously published systems, the timing of the radiation pulse relative to t_d and t_p is not explicitly mentioned. If the radiation pulse occurs after a short delay period following the period t_c , the excess charge carriers will experience the field applied by the electrodes. However, during and following the period t_d , this may no longer be the case because of a non-homogeneous distribution of charge carriers in the bulk solution as explained below. The excess charge carriers are, however, homogeneously produced by the radiation pulse, but the resulting transient electrode current is thus influenced by the overall inhomogeneity of the field in the solution.

The decay period, t_d , can be considered to be due to the formation of a shielding layer near the electrode surface thus progressively reducing the current flow through the cell and thereby modifying the field experienced by the bulk solution. Several processes contribute to the formation of such a shielding layer. In the first instance, a charged double layer is formed (Bockris and Reddy, 1970; Moore, 1972) and secondly, the field is distorted due to separation of charges causing increased concentrations near the electrodes. Finally, these charges are neutralized at the electrodes, giving rise to an increase in concentration of neutral species near the electrodes. It seems that it is this final effect which is primarily responsible for the observed decay and can be thought of as causing a decrease in the active surface area of the electrode.

A very convenient method of overcoming this effect is to increase the active surface area by coating the electrodes with spongy platinum (platinum black) as shown in Fig. 1. This indeed has been used for steady-state conductivity measurements for a long time. However, time resolved measurements have been traditionally performed using bright platinum electrodes with the exception of a cell constructed from carbon-loaded glass (Janata, 1982). Platinum electrodes are very suitable for work with moderately or non-conducting solutions where the current densities are low and t_d is correspondingly long. With highly conducting solutions, the field may be considerably distorted and can give rise to large errors in the measured transient current. Examples of the errors resulting from this field distortion are shown in Figs 2-4. In extreme cases, even a temporary reversal

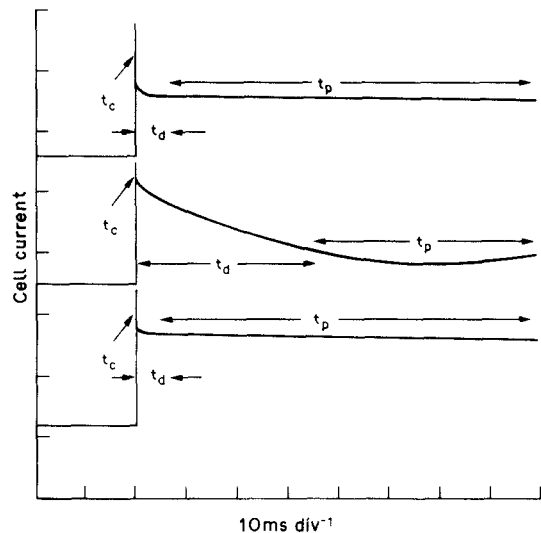


Fig. 1. Kinetics of the current flow through a conductivity cell (cell constant = 0.27 cm^{-1}) in response to a voltage step. (a) Low current density ($100 \times 10^{-6} \text{ M}$ sodium perchlorate), bright platinum electrodes; (b) high current density ($10 \times 10^{-3} \text{ M}$ sodium perchlorate), bright platinum electrodes; (c) high current density, platinum black coated electrodes.

of the polarity of the observed transient current can occur.

The results presented in the subsequent figures were all performed with a balanced detection apparatus similar to that described previously (Vojnovic *et al.*, 1983) using 3.5 MeV electron pulses produced by a Van de Graaff accelerator. Figure 2 shows the neutralization of the radiation-induced charges by excess H_3O^+ ($\text{pH} = 3.1$); this reaction should proceed with a decay time of *ca* 70 ns. In trace (a) the problem has been exaggerated by polarizing the solution for

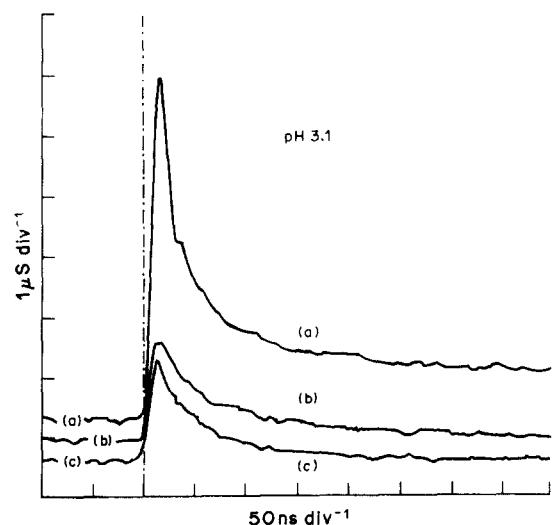


Fig. 2. Changes in conductance in N_2 -saturated water at $\text{pH} 3.1$ following a 5 Gy electron pulse. (a) Bright platinum electrodes, d.c. excitation, 50 ms time delay, (b) bright platinum electrodes, a.c. excitation at 500 Hz, (c) black platinum electrodes, d.c. excitation, 20 ms time delay.

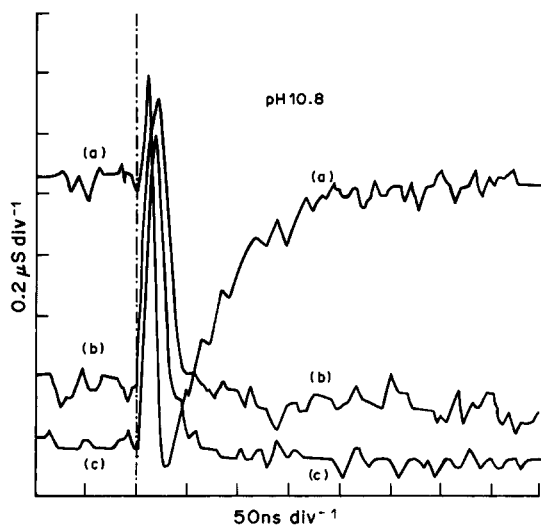


Fig. 3. Changes in conductance in N_2 -saturated water at pH 10.8 following a 4.7 Gy electron pulse. (a) Bright platinum electrodes, d.c. excitation, 50 ms time delay, (b) bright platinum electrodes, a.c. excitation at 500 Hz, (c) black platinum electrodes, d.c. excitation, 20 ms time delay.

50 ms before irradiation. This should be compared with trace (b) where an a.c. sine-wave excitation field is used, synchronized to the electron pulse so that irradiation takes place on the peak of the sine-wave. Following platinization, the problem is largely overcome, trace (c). Figure 3 shows the neutralization reaction in a basic solution. In trace (a), once again the problem has been exaggerated by using a 50 ms delay time. This time quite unexpected kinetics are observed, compared to trace (b), obtained using a.c. excitation and trace (c), using d.c. excitation and black platinum electrodes. The severity of the distur-

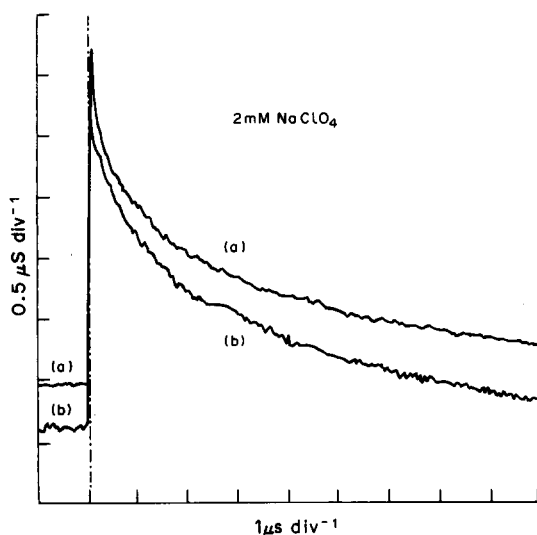


Fig. 4. Increase in conductance in N_2 -saturated near-neutral (pH = 6.1) 2×10^{-3} M sodium perchlorate solution following a 5 Gy electron pulse. (a) Bright platinum electrodes, d.c. excitation, 20 ms time delay (b) black platinum electrodes, d.c. excitation, 20 ms time delay.

tion is larger with increasing current intensities but in most instances the errors become small after several microseconds (Fig. 3).

At times of $< 10 \mu s$ with high conductance solutions, it is desirable to use platinum black electrodes, to apply a low polarizing voltage and to arrange the timing of the electron pulse to be near the start of the period t_d . Clearly as can be seen from Fig. 1, observations at long times require that a long t_d is established and this can only be obtained with coated electrodes.

Similar precautions should be followed when using a.c. excitation. In that case, if the field reversal frequency is low enough (< 1 kHz), significant phase shifts will occur between the applied voltage and background conductance current. Large calibration errors may occur, depending on whether the detection instruments measure the real component (conductance) or admittance.

While a detailed description of all relevant processes which contribute to the polarization phenomenon is not presented here, a relatively simple method to overcome their effect in the case of transient measurements may be applied in pulse-radiolysis work. The electrodes can be coated with platinum black, as described in the Appendix. The measurements of transient conductance changes in highly conducting solutions at times $< 10 \mu s$ should be interpreted carefully and it is necessary to check the condition of the electrodes periodically by monitoring the kinetics of the cell current in response to a voltage step.

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APPENDIX

Platinum electrodes can be covered in platinum "black" by using a solution of 1.5 g chloroplatinic acid and 15 mg lead acetate in 50 ml of distilled water. The electrodes should first

be cleaned in chromic acid and thoroughly washed. The platinizing solution is then introduced into the cell and the electrodes connected to a 3 V d.c. source, capable of supplying in excess of 1 A. The polarity of the supply should be reversed every 30 s and the process continued for 10 min.

The cell should then be thoroughly cleaned in distilled water. A tougher coating may be obtained by repeating the above process but using a 1 M sulphuric acid in place of the platinizing solution.