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Measurement of electrolytic conductivity in highly conducting solutions

ROBERT J. GUANTI,* PATRICK J. MORAN

Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland 21218, USA

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A new technique, suitable specifically for the determination of specific conductivity in highly conducting solution is described. The technique combines the advantages of four-electrode measurement with those of fast current interruption to yield a clear signal, proportional to the resistivity of the solution and independent of any polarization effects.

The conductivity of concentrated aqueous solutions of KOH is measured over a range of temperatures from 25 to 70° C and compared to literature data on the one hand and to measurements with a commercial two-electrode a.c. conductometer on the other. Agreement with literature data is good. Two-electrode a.c. measurements yield consistently lower values because polarization is not eliminated. The technique is simple and easily adaptable for on-line operation in the electrolytic industry where continuous monitoring of the conductivity may be important for process control.

1. Introduction

The limited conductivity of electrolytic solutions is a major cause of energy losses in the electrolytic industry. It is therefore necessary to measure the specific conductivity of the solution and to monitor any changes which may occur during normal operation. A potential drop due to solution resistance also interferes with measurements of electrode kinetics. One of the early methods to determine this IR potential drop is the interruptor technique pioneered by Hickling and Salt [1–3], developed and used extensively by Schuldiner beginning in 1950 [4]. In this method, which is best suited for galvanostatic measurements, the constant current supplied to the electrode is periodically interrupted for a short time and the change in potential is measured. Ideally, the potential should change instantaneously by an amount $V = IR$, followed by a slow, initially linear change associated with discharge of the double layer capacitor through the Faradaic resistance of the interface. In practice the two processes often merge, making it difficult to determine the IR drop accurately.

The specific conductivity of electrolytic solutions can be measured readily with commercially available instrumentation employing an alternating current or potential in the frequency range of 50 Hz to 3.0 kHz. An alternating current or potential is used to minimize polarization effects at the two electrodes. While useful for solutions having a low specific conductivity, accuracy is decreased as the specific conductivity is increased and in highly conducting solutions of importance for the electrolytic industry (e.g. concentrated KOH used in water electrolysers), erroneous results may be obtained. This can usually be overcome by employing a four-electrode system in which the two outer electrodes are used to drive a current and the two inner (indicator) electrodes are used to measure the potential [5–7]. Since no current flows through the indicator electrodes, their interfaces are not polarized and the potential measured between them is solely due to the IR drop caused

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* *Present address*: US Navy David Taylor Naval Ship R & D Center, Bethesda, MD 21402, USA.

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by the current flowing through the two outer (driver) electrodes. While a significant polarization may occur at these electrodes, it will not be part of the measured potential and will hence not affect the measured conductivity.

In the present work the advantages of two existing techniques are combined in the four-electrode d.c. interruptor method for the determination of specific conductivities in highly conducting media. The new technique is applied to the measurement of conductivities in concentrated KOH solutions (up to 35 wt %) over a range of temperatures up to 70° C. Results are in good agreement with best available literature data [8]. The method is suitable for on-line monitoring of conductivities in highly conducting media of interest to the electrolytic industry such as concentrated acids, bases, brines or even molten salts.

2. Experimental details

Two cells were constructed and utilized in this study. The cell used for potassium hydroxide electrolyte experiments is shown in Fig. 1. It consisted of a polymethylmethacrylate rectangular box, 2.5 × 3.0 × 7.5 cm, housing four electrodes. The outer (driven) electrodes were nickel foils. The inner electrodes were nickel screens, 2.5 × 2.5 cm, and were set exactly 2.5 cm apart. The driven electrodes were 2.5 cm wide and 3.0 cm high and the cell was filled to a level of 2.5 cm in each experiment. Nickel could not be employed to determine the cell constant in solutions of KCl since it would be electrochemically dissolved in this medium. For the KCl electrolyte experiments platinum foils, 2.5 × 3.0 cm, were used as the driven electrodes and platinum wires 0.05 mm in diameter were used as the inner electrodes. Again, the spacing between the inner electrodes was exactly 2.5 cm.

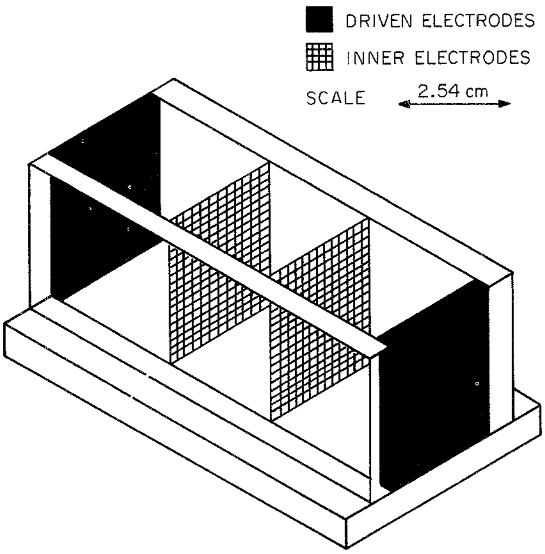

Fig. 1. The four-electrode cell.

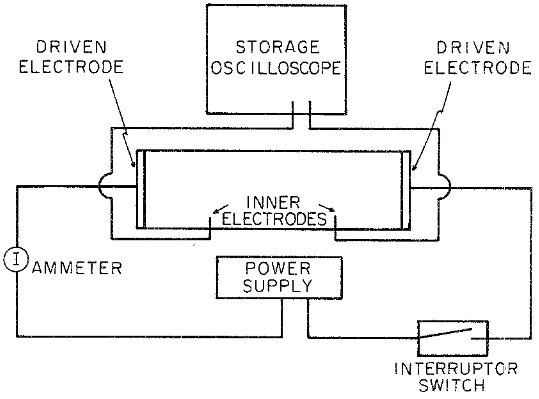

Fig. 2. Block diagram of the measuring circuit.

A block diagram of the circuit used to perform the four-electrode interruptor conductivity measurements is shown in Fig. 2. The circuit consisted of a PAR Model 173 potentiostat used in the constant current mode, a Fluke model 8020A Ammeter and an Electrosynthesis Corp. Current Interrupter switch model 260 (switching time $< 5\,\mu s$). A Nicolet Model 204-A Digital oscilloscope was employed to measure the change in potential between the inner electrodes caused by opening the interruptor switch.

Temperature was controlled by means of a Thermonic Model 1480 water bath, temperature-controlled to ±0.2° C. Uniformity of temperature was measured with a Yellowstone Scientific Instrument Model 32 Digital Temperature Probe which was removed from the cell during measurement of conductivity. A YSI Model 35 Conductance Meter was used for comparison and calibration purposes. Solutions were made from Baker Reagent grade KOH and dionized water. The concentrations studied were 5.49, 6.85 and 8.33 M, corresponding to 25, 30 and 35 wt %. The cell constant was determined with KCl in

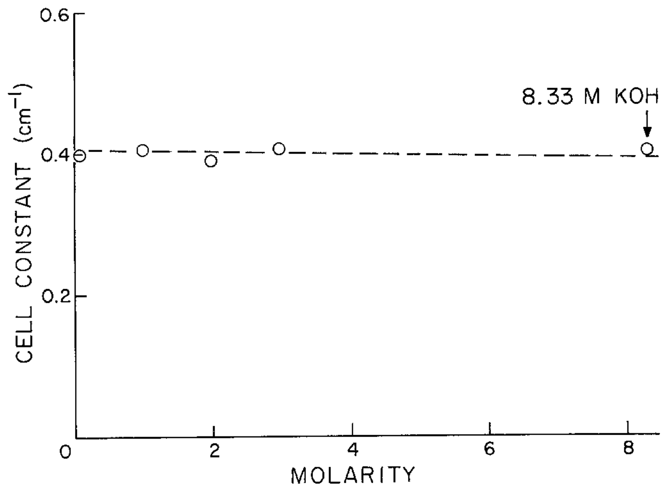

Fig. 3. The cell constant as a function of electrolyte concentration for potassium chloride at 25° C.

the concentration range of 0.100–3.00 M and two temperatures (21° C, 58° C).

3. Results and discussion

3.1. *Cell constant*

The cell constant can be calculated from the geometry of the cell as 0.4 cm^{-1}. It should be noted that because of the simple geometry involved the cell constant depends only on the distance between the inner electrodes and is independent of their position in the cell. This is because the equipotential lines in the cell are parallel to the driving electrodes and therefore the voltage gradient, change in voltage per change in distance along the length of the cell, is constant along the length except very near the driving electrode surfaces. Fig. 3 shows the values of the cell constant, measured at 25° C with solutions of KCl, in the range of concentration of 0.1 to 3.0 M. An additional measurement in 35 wt % KOH, employing the literature value of 0.6 $\Omega^{-1}\mathrm{cm}^{-1}$ reported by Klochko and Godneva [8], yields the same cell constant. The value of 0.4 cm^{-1} obtained experimentally is equal to that calculated from cell geometry.

The conductivity of 0.1 M KCl was also measured by the four-electrode interruptor method over a range of frequencies (2 Hz to 5 kHz) at four different temperatures and was shown to be independent of frequency, as seen in Fig. 4.

3.2. *The conductivity of KOH solutions*

The specific conductivity of 5.45 M KOH is shown in Fig. 5 as a function of temperature. Measurements taken with the four-electrode current interruption method are compared to those obtained by a conventional conductometer. The difference is significant and shows the inadequacy of a conventional two electrode conductometer for the determination of the conductivity in highly conducting solutions. A similar discrepancy was observed in all KOH solutions tested. The specific conductivities of three solutions of KOH (5.49, 6.85 and 8.33 M) are compared in Fig. 6 over the same range of

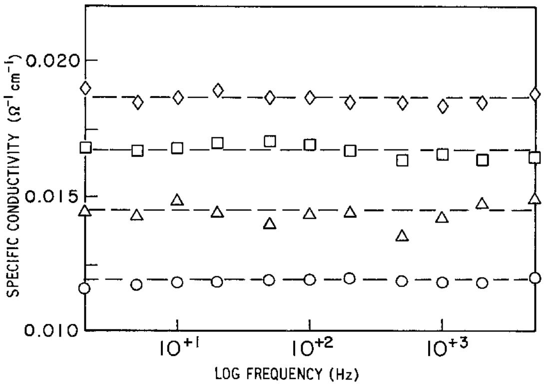

Fig. 4. Frequency dependence of the conductivity of 0.100 M KCl at four temperatures: ○, 23° C; △, 46° C; □, 51° C; ◇, 59° C.

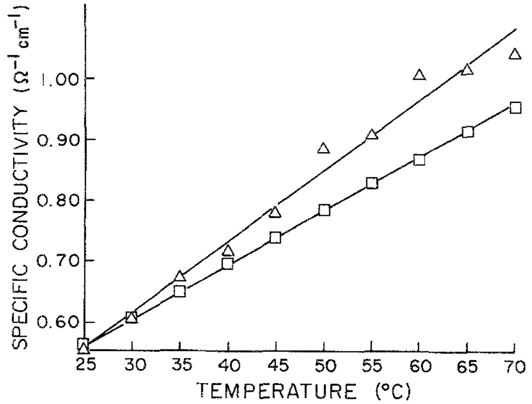

Fig. 5. Comparison of conductivities measured with a conventional two-electrode conductometer and the four-electrode current interruptor technique for 25 wt % KOH, as a function of temperature. Average of six tests. △, current interruption; □, conductometer.

temperature. Each point in the last two figures represents the average of six measurements.

Klochko and Godneva [8] reported the concentration dependence of the specific conductivity of aqueous KOH solutions at different temperatures. A maximum in specific conductivity is observed at 27 wt % at 25° C which shifts to 32 wt % at 75° C and to even higher concentrations at elevated temperatures. The results given in Fig. 6 show no significant difference between the specific conductivities at 30 and 35 wt %, indicating that the maximum in conductivity should be between these two concentrations, throughout the temperature range studied. Detailed comparison shows that the present results are slightly lower (2–4%) than those given in the literature at 70° C. At 25° C the difference increases up to 10% in 25 wt % but is negligible at 35 wt %.

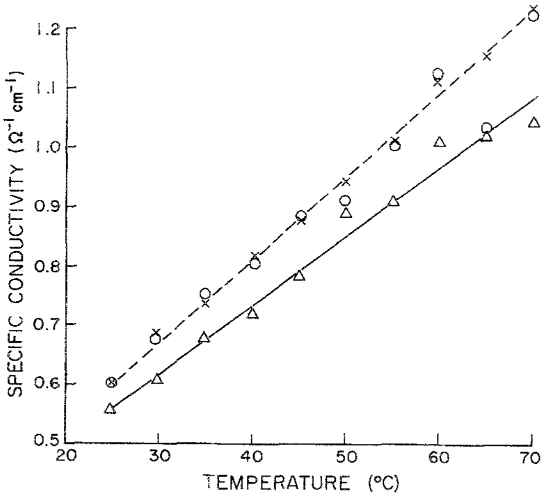

Fig. 6. Specific conductivities of KOH solutions as a function of temperature. △, 25 wt %, 5.49 M; ○, 30 wt %, 6.85 M; ×, 35 wt %, 8.33 M. Dashed line: 30, 35 wt % KOH. Solid line: 25 wt % KOH.

3.3. *The effect of CO_2 on the specific conductivity*

Absorption of CO_2 in alkaline solution can be a major source of error in determining the specific conductivity and an important factor in the decrease in conductivity with time in industrial processes. To test for this effect we compared the specific conductivity in carbonate-free KOH solutions with the results obtained after bubbling CO_2 through the solution for 15 min. Baker 'carbonate-free' KOH electrolytes were used and the concentrations tested were 1.0, 5.45 and 6.85 M. Solutions were prepared by diluting the 6.85 M stock solution with dionized water, which had been boiled for 30 min to eliminate CO_2, and allowed to cool under a positive pressure of purified nitrogen.

A somewhat similar experiment, in which 30 wt % KOH was diluted with either pure, CO_2-free water or with 2.11 M K_2CO_3, was reported in the literature [8]. Addition of carbonate caused a steep decrease in specific

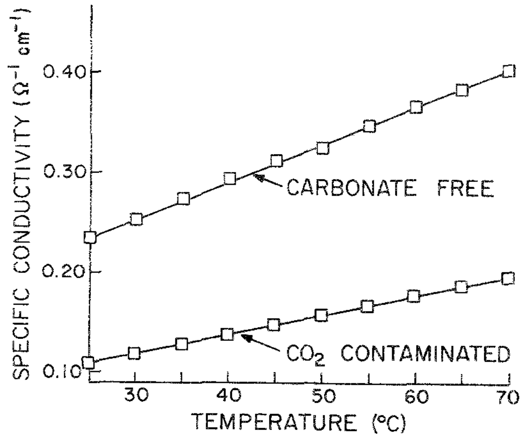

Fig. 7. The effect of absorbed CO_2 on the specific conductivity of 1.0 M KOH.

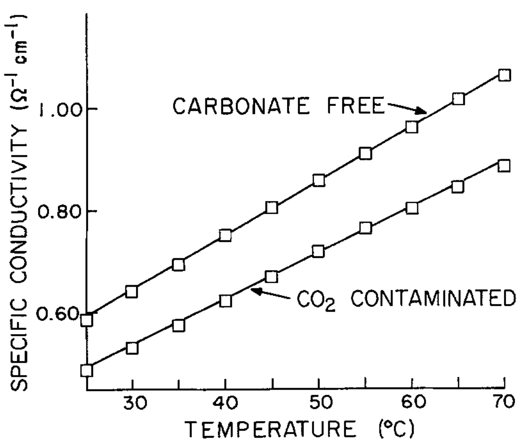

Fig. 8. The effect of absorbed CO_2 on the specific conductivity of 6.85 M KOH.

conductivity due to the lower equivalent conductivity of the $CO_3^=$ ion, compared to OH^-.

Results for 1.0 and 6.85 M KOH are shown in Figs 7 and 8, respectively. As expected, the effect of CO_2 absorption is more pronounced in the more dilute solution since the relative change in concentration of KOH is larger. In both cases the effect is quite large, pointing to the importance of monitoring and controlling the concentration of CO_2 during industrial electrolytic processes.

4. Conclusions

A simple and convenient constant current four-electrode interruptor technique has been described for the measurement of specific conductivity in highly conducting media. The cell constant was found to be invariable over a range of concentrations (0.1–3.0 M KCl; 1.0–8.33 M KOH), frequencies (2–5 × 10^3 Hz) and temperatures (22–55° C). The measurement is not affected by electrode polarization and is of short duration, making it useful for on-line application in many industrial electrolytic processes, including those employing molten salts at elevated temperatures. The results obtained for three concentrations of KOH (25, 30, 35 wt %) over a range of temperatures from 22° to 70° C are 2–10% lower than literature data, where available. Monitoring and control of the concentration of CO_2 is shown to be essential, since the specific conductivity is significantly reduced when CO_2 is absorbed.

Acknowledgement

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