



# Development of in situ a.c. impedance measurement system under constant-current conditions and its application to galvanostatic discharge of electrolytic manganese dioxide in alkaline solution

K. Tachibana<sup>\*</sup>, K. Matsuki

*Department of Materials Science and Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan*

Received 22 August 1997; accepted 18 December 1997

---

## Abstract

An inexpensive a.c. impedance measurement system to elucidate the solid-phase electrochemical reactions inside the active materials of batteries during charge and discharge has been developed by using a cheap galvanostat and a personal computer. In order to develop a simple, in situ, a.c. impedance measurement system for evaluating cells, the impedance of manganese dioxide in alkaline solution under constant-current discharge has been measured. To obtain the impedance, a discrete sinusoidal current is superimposed on the cell under the constant-current polarization, and the resulting transfer function is calculated by a single, sine wave, correlation method. Software developed in this study makes it possible to measure the impedance without using a frequency-response analyzer. A large sinusoidal current of magnitude up to that of the discharge current can be superimposed while keeping the sinusoidal potential response in the linear range, and this enables reliable impedance measurements to be conducted. The impedance and frequency characteristics thus obtained reflect well the discharge behaviour of manganese dioxide in alkaline solution. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* In-situ impedance; MnO<sub>2</sub>; Galvanostatic condition; Alkaline manganese battery

---

## 1. Introduction

Measurements of a.c. impedance at open-circuit potential are widely used to evaluate electrodes in batteries. For example, the a.c. impedance of lithium deposition in an organic solvent has been analyzed [1,2] by assuming an equivalent circuit, and then the charge-transfer process of the lithium deposition has been discussed. In general, the frequency dependency of the a.c. impedance is used in the analysis because it may be suitable for the elucidation of heterogeneous reactions at the electrode/electrolyte solution interface. Nevertheless, the interesting frequency range of the a.c. impedance for the electrochemical reaction inside the solid phase is usually located at very low frequencies due to the small diffusivity of electroactive species inside the solid and hence, much simpler measurement/analytical methods may be necessary. When evaluation of battery performance is the main subject of the measurements, it is better to use a galvanostatic operation in the analysis of the charge–discharge rate and/or the

presence of hysteresis. Furthermore, it is desirable to construct a flexible measurement system with programmable computer control, since measurement of the charge–discharge process of batteries is time-consuming.

In order to evaluate the electrode further, impedance measurements should be carried out in situ, i.e., under the passage of current during the course of battery charge–discharge. Osaka et al. [3] have reported that in situ, a.c. impedance measurements during galvanostatic polarization is very effective for rapid evaluation of the surface conditions of lithium anodes during charge and discharge processes. Nevertheless, the use of an in situ method intensifies the problem of errors caused by the nonstationary behaviour of the battery. The a.c. value of the current has to be a compromise between the general requirement for small signal deviation and data quality that is directly related to the amplitude of the a.c. signal.

In this paper, we report a flexible and simple, in situ, a.c. impedance measurement system. This is a computer-assisted system with software to measure the cell impedance without using an expensive frequency-response analyzer. An electrolytic manganese dioxide (EMD)/al-

---

<sup>\*</sup> Corresponding author.

kaline cell is chosen as a test cell because of the numerous studies of the discharge characteristics that have been performed to date [4].

**2. Experimental**

*2.1. Measurement system*

A block diagram of the impedance measurement system is shown in Fig. 1. The software developed in this study consists of several functions such as measurement of discharge curves, generation of input sine wave, and acquisi-

tion of the response signal. This software has been coded in BASIC (MS Visual Basic 2.0j, Microsoft) and C (MS Visual C++ 1.0j, Microsoft) languages on a commercially available multitask operating system (MS-Windows 3.0j Microsoft). An AD/DA converter ( $\pm 10$  V range in 12-bit resolution, Contec) is attached as the interface between a personal computer (PC-9801 Ap, NEC) and a potentiogalvanostat (HA161 Hokuto denko). The discharge test was conducted at  $1.0 \text{ mA cm}^{-2}$  with a superimposed sinusoidal current of 1 Hz at  $1.0 \text{ mA cm}^{-2}$  at adequate time intervals. The impedance was calculated by a single, sine-wave correlation method [5] from the responses of an amplitude and a phase that were stored in

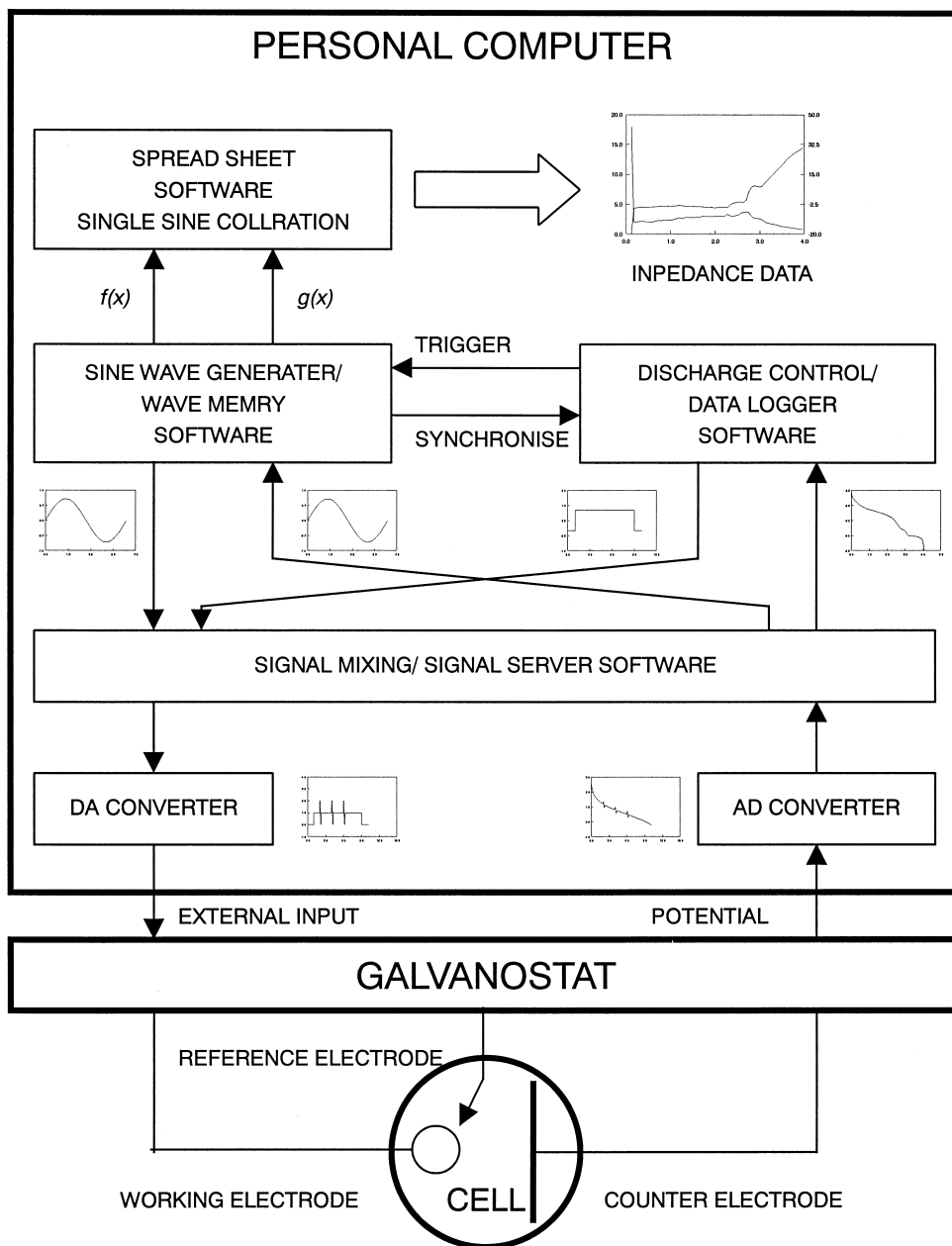


Fig. 1. Schematic diagram of impedance measurement system.

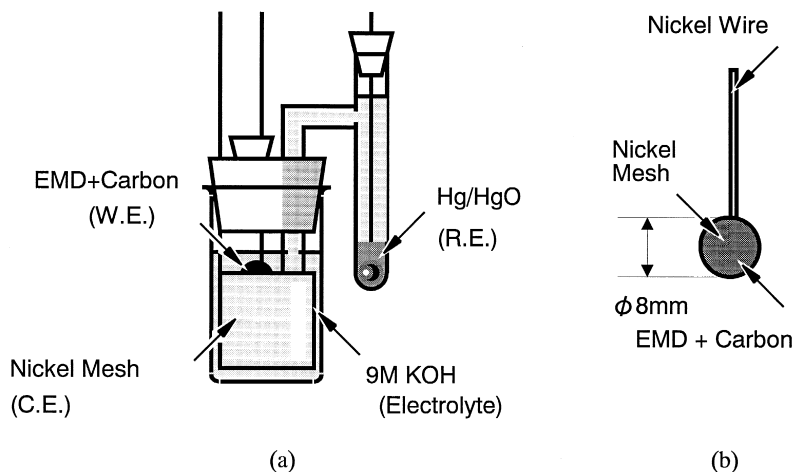


Fig. 2. Schematic of: (a) experimental cell; (b) test electrode.

the buffer memories. MS-Excel 5.0 (Microsoft) spreadsheet software was used for the calculation.

## 2.2. Cell system

Schematics of the glass test cell and the test electrode, which is basically the same as that of Bai et al. [6], are given in Fig. 2. The positive electrode had about 30 mg  $\text{MnO}_2$  and was formed into pellets of about  $101 \text{ mm}^2$ , which were made from a mixture of EMD (IC 21) with graphite (Lonza, KS-15) in a 1:1 ratio by weight. A 10 wt.% Teflon suspension (Du-Pont-Mitsui Fluoro 30 J) was added as a binder, then the mixture was kneaded in a motor with a pestle to form rubber-like films, and then pressed on to both sides of a nickel mesh using a plastic mould and a hand press. A nickel gauze electrode was employed as the negative plate. The electrolyte was 9 M KOH and the reference electrode was a Hg/HgO system in the same solution. Measurements were performed in an air thermostat at  $25^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Characteristics of measurement system

The transfer function between the potential response and the sinusoidal current superimposed on the constant discharge current may correspond to the impedance when the system is linear. Therefore, it is important to check the linearity range of the system and test cells. A typical discharge curve for the EMD in 9 M KOH at  $1 \text{ mA cm}^{-2}$  is shown in Fig. 3. The electrode potential shifts gradually in a cathodic direction with the discharging process to around  $-0.2 \text{ V}$ . A short potential arrest appears just before the discharge depth at an electron. After this, a long potential arrest due to the dissolution of  $\text{Mn(III)OOH}$  is observed at around  $-0.4 \text{ V}$ . This discharge behaviour is a typical response of EMD in alkaline solution.

In general, an electrochemical system can be considered as a linear system if the amplitude of the perturbation signal is sufficiently low [7]. Since an AD/DA converter has been used in this study, an unavoidable discrete noise (digitizing noise) generated from the converter will cause the low measurement precision. Therefore, it is necessary for the superimposed sinusoidal current to be as large as possible up to the discharge current ( $4 \text{ mA cm}^{-2}$ ) while keeping the system in a linear condition. Thus, the linearity range was checked prior to the detailed impedance analysis; the resulting potential response is shown in Fig. 4 for the same amplitude of current perturbation signal ( $4 \text{ mA cm}^{-2}$ ) and discharge current density. The amplitude of the potential response is about 10 mV. Such a value might be due to the small internal impedance required for batteries.

The effect of the amplitude of the superimposed sinusoidal current (in the range  $0.5$  to  $10 \text{ mA cm}^{-2}$ ) on the potential response, is shown in Fig. 5. A linear relationship is obtained and this indicates that the system is linear over a wide amplitude range of sinusoidal current. In addition, it has been confirmed that the superimposing of such a

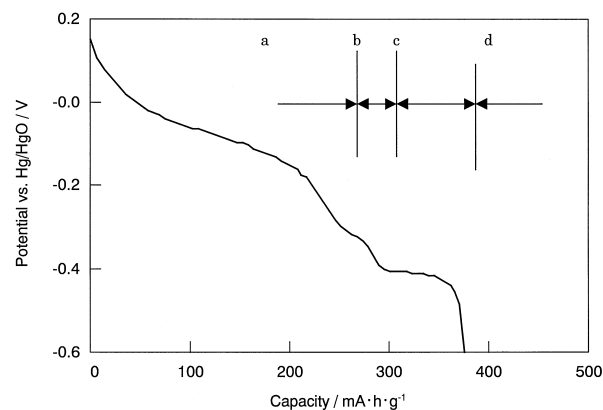


Fig. 3. Discharge curve of EMD in 9 M KOH at  $25^\circ\text{C}$ ; current density =  $1 \text{ mA cm}^{-2}$ .

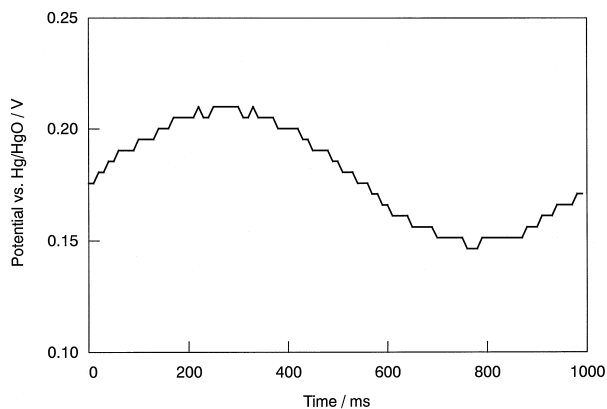


Fig. 4. Potential response curve to sinusoidal current wave at 1 Hz superimposed on a constant-current discharge. Amplitude of sinusoidal current wave is same as that of the discharge current. Other experimental conditions as in Fig. 3.

large sinusoidal current does not exert any appreciable influence on the discharge characteristics.

### 3.2. Impedance curves of EMD during constant-current discharge

In order to minimize the influence of the superimposing sinusoidal current on the discharge reaction, the current was applied for only 1 s for every 10 min. The impedance and phase, together with the discharging curve, during discharging EMD at  $4.0 \text{ mA cm}^{-2}$  in 9 M KOH, are shown in Fig. 6. Kozawa and Power [8] suggested that the cathodic reduction takes place by the incorporation of protons and electrons into the  $\text{MnO}_2$  lattice during region a to c of the discharge curve, i.e.,



According to Kozawa [9], region a to b in the first step corresponds to the homogeneous reduction with no change in the lattice structure. The region b to c corresponds to homogeneous reduction with possible slight deterioration

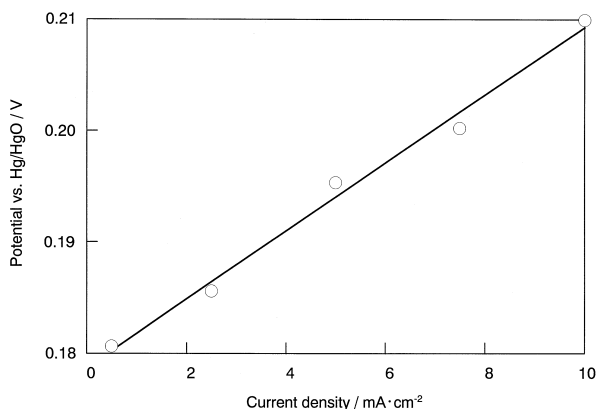


Fig. 5. Relationship between amplitude of superimposed sinusoidal current ( $0.5\text{--}10 \text{ mA cm}^{-2}$ ) and that of potential response.

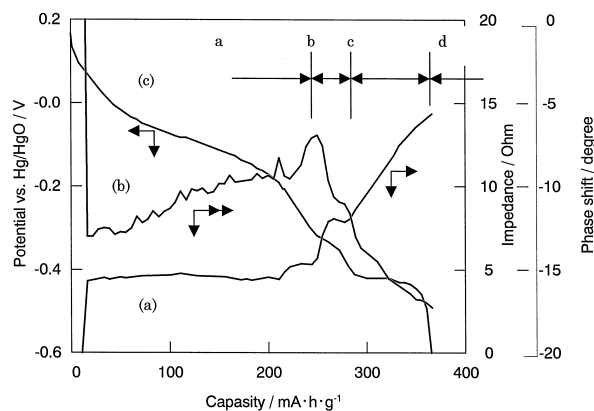
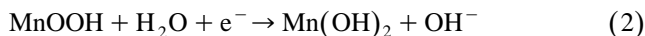


Fig. 6. Change in (a) impedance  $|Z|$  and (b) phase shift  $\phi$  during discharge of EMD at  $1 \text{ mA cm}^{-2}$  in 9 M KOH solution; (c) discharge curve.

in the lattice structure, while the region c to d (second step) corresponds to the heterogeneous phase reduction:



In the course of discharge process b to c, a small plateau potential appears at around 0.8 electron discharge, where a milky turbidity formation was found to be started at the surrounding EMD cathode and then concentrated slowly with changing colour to brown. This behaviour indicates that reaction (2) may have partly occurred. In the c to d region where, the discharge reaction proceeds to one electron or above, the plateau potential has a ripple, which seems to respond to the superimposed sinusoidal current.

Next, the impedance behaviour measured during the discharge will be considered. In the region a to b (homogeneous phase reduction) in the discharge curve, the impedance  $|Z|$  is almost unchanged, while the phase difference  $\phi$  increases slowly with time, and accordingly the capacitive component of the EMD electrode increases. In the region b to c (homogeneous reduction with possible slight deterioration in the lattice structure),  $\phi$  decreases rapidly after having reached the small plateau in the discharge potential (a heterogeneous phase reaction may be occurring). On the other hand,  $|Z|$  increases in the region b to c region and the following c to d region. It can be seen that the ripple appeared in the discharge curve in the c to d region with increasing the impedance. The above findings provide a clear indication that the a.c. impedance thus obtained under galvanostatic conditions agrees well with the discharging reaction inside the solid phase of the electroactive materials.

### 3.3. Frequency characteristics of the impedance

The frequency dependence of impedance was measured in the frequency range 0.1 to 100 Hz. The frequency range was very limited due to the sampling time limitation of the A/D and D/A conversion of the computer used here for

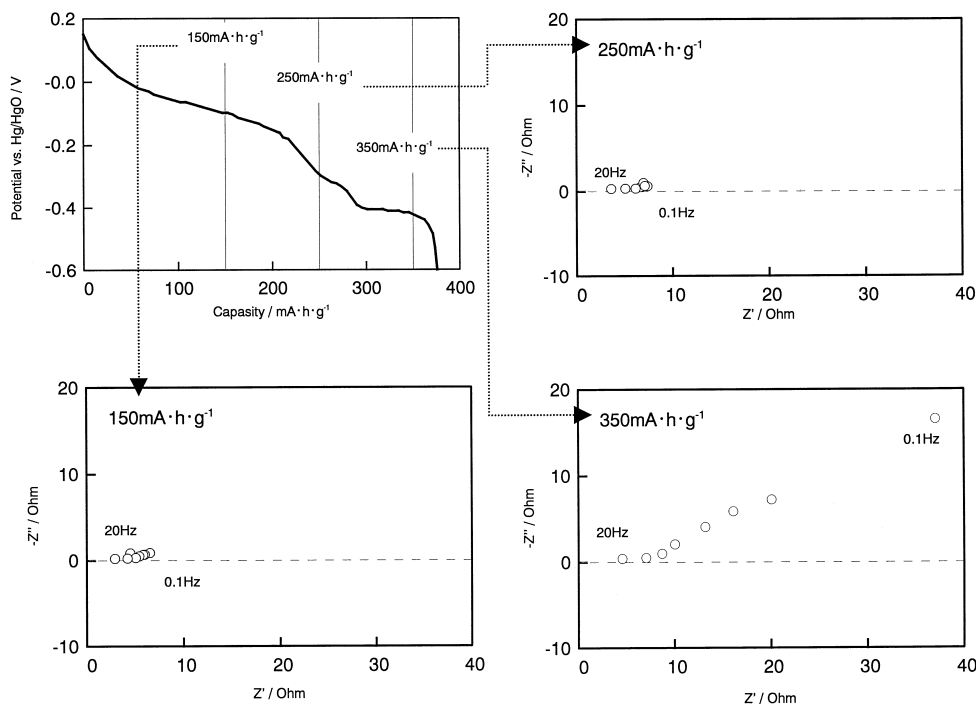


Fig. 7. Cole–Cole plots obtained at several points of discharge states. Discharging condition as in Fig. 3.

the high frequency end, while the lower frequency end was chosen at 0.1 Hz to prevent the effect on the discharge reaction by superimposed sinusoidal current.

Cole–Cole plots of the impedance measured at  $-0.2$ ,  $-0.3$  and  $-0.4$  V on the discharge curve of the EMD are shown in Fig. 7. Since the test cell gave highly reproducible discharge data [10] and the computer control program did not allow simultaneous measurement of all the impedance spectra, the EMD test electrode was replaced with a fresh electrode for each frequency. The Cole–Cole plots are approximately constant at a discharge potential of  $-0.2$  and  $-0.3$  V at which a homogeneous reduction is taking place. By contrast, the plot shows a clear frequency dependence at  $-0.4$  V at which a heterogeneous reduction is proceeding. This suggests the possibility of a ionic diffusion control in the  $\text{MnO}_2$  lattice.

These results support the previously reported cathodic reduction mechanism of  $\text{MnO}_2$  in alkaline solution [7,8] in that it agrees well with the reaction mechanism whereby a homogeneous reaction in the solid phase is changed to a heterogeneous reaction at the solid/electrolyte interface. Thus, it is concluded that the a.c. impedance measurement under galvanostatic conditions is a powerful tool for analyzing the electrochemical reaction inside the solid phase of electroactive materials. The a.c. impedance measurement system developed in this study provides an inexpen-

sive but quite flexible measurement system since no additional equipment is required. Furthermore, the flexible programmability of the system enables long-term measurements such as cycle-life tests of batteries. Work concerning the role of  $\text{MnO}_2$  in the anodic process is in progress.

## References

- [1] J.G. Thevenin, R.H. Muller, *J. Electrochem. Soc.* 134 (1987) 273.
- [2] T. Osaka, T. Momma, K. Nishimura, T. Tajima, *J. Electrochem. Soc.* 140 (1993) 2745.
- [3] T. Osaka, T. Momma, T. Tajima, *Denki Kagaku* 62 (1994) 350.
- [4] T.A. Andersen, in: R.E. White, B.E. Conway (Eds.), *Modern Aspect of Electrochemistry*, No. 30, Chap. 4, Plenum, New York, 1996.
- [5] C. Cachet, H. Cachet, J.C. Lestrade, *Electrochim. Acta* 19 (1974) 891.
- [6] L. Bai, D.Y. Qu, B.E. Conway, Y.H. Zhou, G. Chowdhury, W.A. Adams, *J. Electrochem. Soc.* 140 (1993) 884.
- [7] F. Mansfield, W.J. Lorenz, in: R. Varma, J.R. Selman (Eds.), *Characterization of Electrodes and Electrochemical Process*, Wiley, New York, 1991, p. 581.
- [8] A. Kozawa, R.A. Power, *J. Electrochem. Soc.* 113 (1966) 870.
- [9] A. Kozawa, in: J. Tompson (Ed.), *J. Power Sources* 7 (1979) 485, Academic Press, London.
- [10] K. Tachibana, K. Matsuki, A. Kozawa, *Prog. Batteries Battery Mater.* 16 (1997) 322.