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DIGITAL SIGNAL ANALYSIS OF MOLTEN SALT ELECTROLYSIS CELLS

R.P. Singh, J.H. Flint, and D.R. Sadoway

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

The electrowinning of manganese from molten $MnCl_2$-alkali chloride electrolytes is being studied by digital signal analysis through the computation of the fast Fourier transform of cell voltage. Electrolysis is conducted galvanostatically. With the aid of a reference electrode, the anode versus reference voltage and cathode versus reference voltage are sampled. The relationship between physical processes occurring in the cell and frequency spectra of the measured voltages is being investigated.

Introduction

The deposition cycles in industrial electrolytic processes are very long, running from several days to several weeks. To achieve higher efficiency and produce better quality deposits make it imperative to develop some way to monitor these processes continuously on line. Early detection of the changes in the operating parameters can serve as the basis for process control. The purpose of the present research is to explore the possibilities of diagnosing cell performance by digital signal analysis using fast Fourier transform of electrical characteristics of an operating cell. The physical system under investigation is the molten salt electrolysis of manganese from $MnCl_2$-alkali chloride melts.

When a metal electroreduction cell is operating, the measured cell voltage, E_{cell}, can be divided into the following components:

$$E_{cell}=E_{rev}+E_{ohm}+E_{contact}+\eta_{cathode}+\eta_{anode}$$

where E_{rev} is the reversible cell potential, E_{ohm} is the ohmic drop across the electrolyte and may include the iR drop of the electrolyte itself and a contribution from gas bubble at the electrodes, $E_{contact}$ is the contact resistance at the points where the conductors from the power supply are connected to the electrodes, and η is the overvoltage at the specified electrode. Depending upon the cell design and operating conditions, the magnitude of each term will vary. For example, during gas evolution at the anode in an electrowinning operation bubbles of chlorine displace the electrolyte from the electrode (1). This makes it more difficult to pass current; thus, the cell impedance rises. When a gas bubble detaches, the electrolyte then flows back to make electrical contact with the electrode again, and the cell impedance drops. If such a cell were being driven galvanostatically, the rise and fall of cell impedance would be reflected in the cell voltage (2). This fluctuation in cell voltage due to gas evolution is expected to have its own characteristic electrical signature, which is difficult to identify when seen against a background of normal voltage fluctuations on a plot of voltage versus time. However, by digital signal processing it is possible to suppress random fluctuations and through spectrum analysis reveal the electrical signals associated with physical processess occurring in the cell. In other words, by the use of fast Fourier transform, it may be possible to elucidate in frequency domain certain periodic phenomena that cannot be observed in time domain.

It is well known that electrodeposition under conditions of diffusion control or at high current densities leads to rough deposits (3). The addition of leveling agents leads to smoother deposits by shifting the control of the process from diffusion to another mechanism, possibly electron transfer or surface attachment (4). Under diffusion control, variations in the thickness of the boundary layer, due to fluid flow in the cell, are reflected in the fluctuations of the cell voltage. This is not the case when the process is not mass transfer controlled. Thus the addition of leveling agents is expected to decrease the level of fluctuations in the cell under otherwise identical fluid flow conditions (5). This change in the amplitude of fluctuations or noise should be reflected in the amplitude/power spectrum generated by fast Fourier transform, and thus could serve as the basis for controlling the concentration of leveling agent in the bath and the quality of the deposits. This change in amplitude spectrum has been noticed in our previous studies (6). The present work seeks to extend the application to electrodeposition in molten salts (7).

The occurrence of noise, fluctuations, or oscillatory phenomena in

aqueous electrochemical systems has long been reported in the literature (8) There has been a renewed interest in this topic due to the availability of powerful, compact digital computational equipment. A theoretical treatment of noise has been presented by Fleischmann et al. (9). Their analysis is based on the statistics of ensemble of transients and stationary states. Other researchers from the Paris school have also studied electrochemical noise with respect to electrocrystallisation and structure of electrodeposite metals (10). In their study of electrodeposition of zinc they found that the power of electrochemical noise was higher for rougher deposits. However, the addition of leveling agent decreased the noise power (11). Bertocci et al. (12,13,14) and Hladky and Dawson (15) have correlated the amplitude of current fluctuations and spectral density plots of electrochemical noise to breakdown of passivation film and to pitting in metals. Dawson et al. have even used on line monitoring of electrochemical noise in pilot plants to assess the corrosion rate and to identify the presence of general or localized corrosion processes (16). Similarily, a few attempts have been made to study the fluctuations in cell voltages in electrochemical cells to control leveling agent, bath temperature, and cell shorting (17). This has been tried even in Hall cells to help predict the occurrence of the anode effect (18,19). However, there are no reports of applications of digital signal processing of cell currents/voltage using fast Fourier transform for cell diagnostics and control in metal producing cells.

Experimental

The salts used in the present study had to be treated to get rid of moisture and hydrolysis products. These, if present, will interfere with the electrolysis and attack the fused quartz crucible. Analytical grade $MnCl_2$ and alkali chlorides were purchased. Sodium chloride was dried by slowly heating to 500°C under vacuum for about 24 hours. $MnCl_2$ was dried by slow heating to 500°C under vacuum for about 36 hours and then subliming it under vacuum.

Pure α-manganese, which is the stable form at room temperature, is brittle and virtually impossible to machine. In order to make manganese electrodes, an alloy containing 3-4% Cu was prepared. The copper stabilizes the high temperature γ phase which is ductile at room temperature and could be machined easily. Copper being more electropositive than manganese will not participate in electrolysis.

The silver-silver chloride electrode is used as a reference electrode. It consists of a silver wire attached to a fine silver mesh immersed in a melt of silver chloride dissolved in the same supporting electrolyte as used in the main cell. The mesh provides a larger surface area for Ag/Ag^+ reversible reaction and was found to help in attaining stable voltage readings. The electrical contact is established by a fine capillary formed by collapsing a fused quartz tube onto asbestos fiber.

Figure 1 shows the main electrolysis cell consisting of a fused quartz tube 4" in diameter with a water cooled brass cap. The brass cap has ports for electrodes, a thermocouple, reference electrodes and argon gas inlet and outlet. Also ports are provided for introducing the electrodes for pre-electrolysis if needed. The electrolyte is contained in a fused quartz crucible 7" tall and 3.75" in diameter.

A typical experiment consists of charging the crucible with weighed amounts of salts in a glove box and lowering the crucible into the cell. The cell is transferred to the window furnace, immediately capped and evacuated. The melting and electrolysis are carried out under an atmosphe

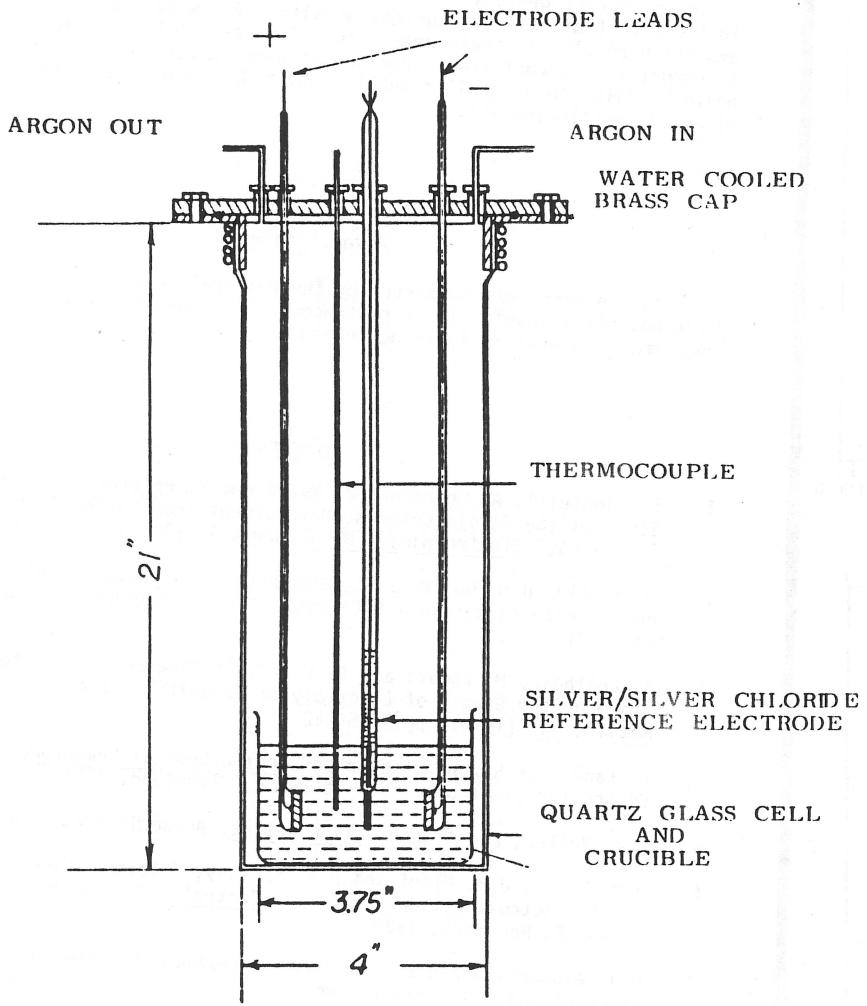

Figure 1. Cell

of dried and oxygen free argon. As soon as the salts have melted, the electrodes are lowered into the melt and galvanostatic electrolysis begins. During electrolysis three channels of the A/D converter of the computer (Digital Equipment Corp., MINC11/23) are used to sample the voltage of the anode with respect to reference, the voltage of the cathode with respect to reference, and the voltage across the cell, i.e. anode vs. cathode. Before sampling by the computer, these voltages are passed through a preamplifier with a d.c. offset and a low pass filter set at 10 Hz (Fig. 2). The sampling rate is 20 Hz. In one sweep 512 samples are collected per channel. As the electrolyte is transparent, any interesting phenomena occurring can be filmed through the window in the furnace. The deposits are examined later by SEM.

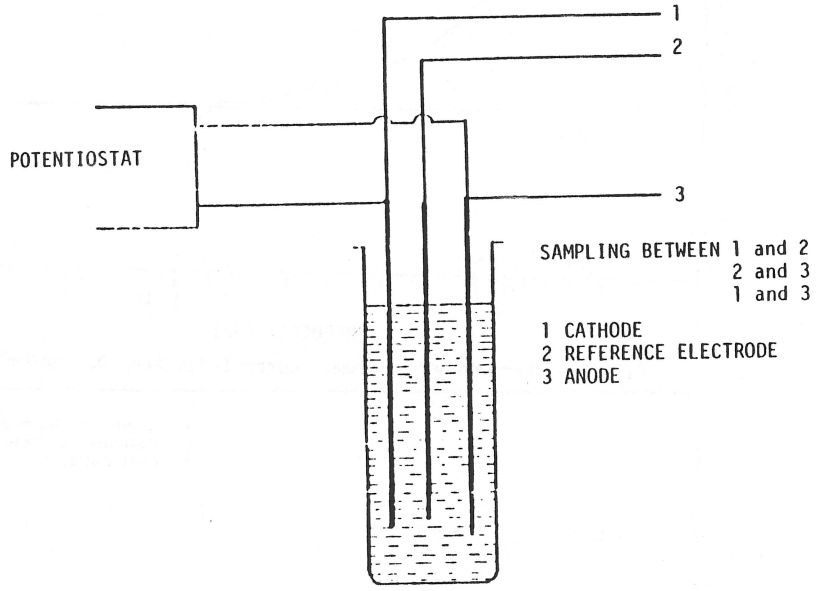

Figure 2. Sampling Diagram

Results and Discussion

The preliminary results of our study demonstrate that it is imperative that a reference electrode be employed to distinguish the cathodic and anodic processes from each other. The cell voltage measured between anode and cathode is confounded and mixes the information about the processes occurring at each of these electrodes.

Figure 3 shows a typical amplitude spectrum obtained during an electrowinning experiment. In this case, a ¼" diameter graphite anode and 3/16" by 5/16" rectangular Mn-Cu cathode were used. Melt composition was 20 mole percent $MnCl_2$ in NaCl. Temperature was held at 800 ±3°C. The melt was pre-electrolyzed for 3 hours using graphite electrodes. During electrowinning the current density was controlled at 9.3 mA/cm^2.

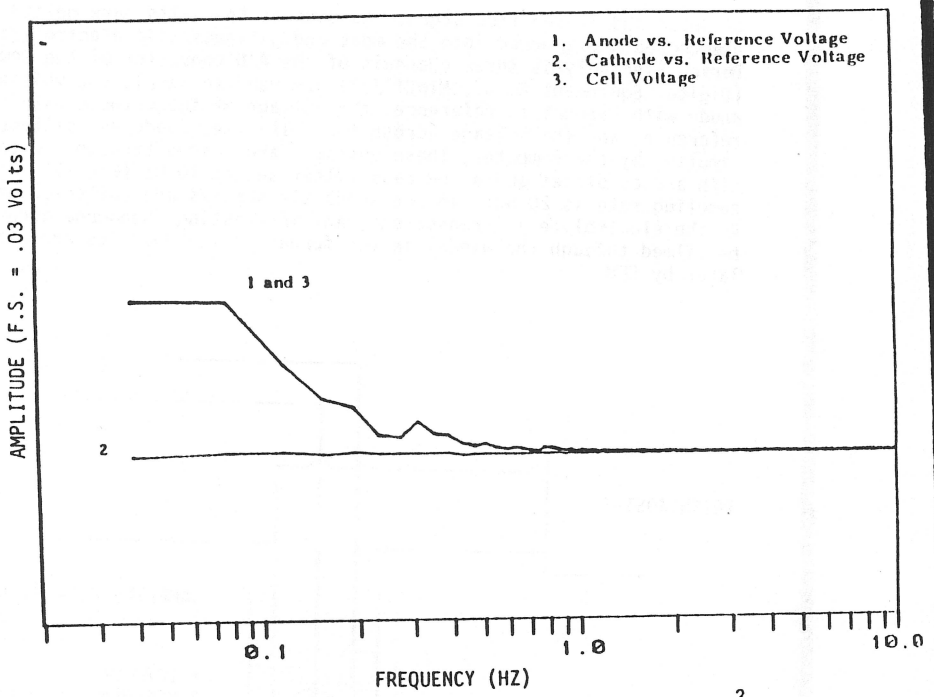

Figure 3. Frequency Spectrum. Current density: 0.3 mA/cm^2

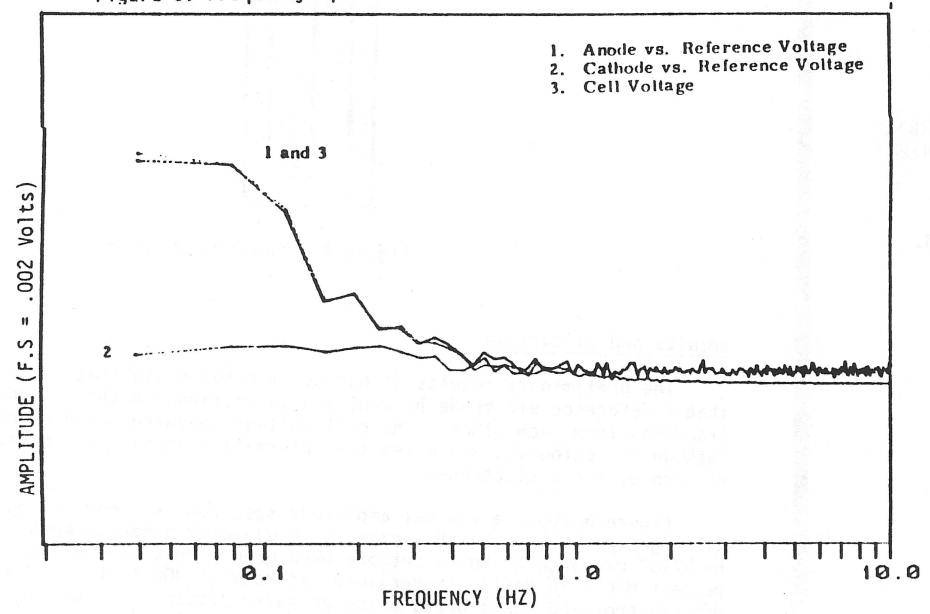

Figure 4. Frequency Spectrum. Current density: 18.6 mA/cm^2

The fluctuations in electrode potential (voltage) occur at low frequencies These fluctuations happen mainly at the anode. At the cathode the fluctuations are comparatively negligible.

When the current density in the cell was increased to 18.6 mA/cm2 the spectra of Figure 4 were obtained. It appears that the amplitude of anode fluctuations when measured against the reference electrode is much higher at lower current density than at higher current density. This may be due to the fact that at lower current density the low rate of chlorine gas evolution results in coalesence into a few large bubbles which severely interrupt the current flow. Perhaps at high current density there is more uniform evolution of smaller bubbles which detach with ease and cause less of a voltage fluctuation.

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