JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 895–900

Measurements of a.c. impedance of sodium–sulphur cells with symmetric and asymmetric resistance behaviour

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Received 15 August 1984; revised 23 October 1984

Measurements of a.c. impedance in the frequency range 10^{-2} Hz $\leqslant f \leqslant 10^4$ Hz were performed on laboratory sodium–sulphur battery cells with symmetric and asymmetric internal resistance behaviour. The impedance spectra of the symmetric cells show only resistive behaviour in the whole frequency range studied. The resistance determined from these spectra is equal to the bulk resistance of the solid electrolyte. In contrast, the impedance of the asymmetric cells is characterized by different high-frequency capacitive and low-frequency inductive behaviour depending on the value of the d.c. current applied. In this case the impedance spectra are very similar to those often observed at metal passivation processes in electrolyte solutions. It is shown that the results obtained can be qualitatively interpreted by a model including the existence of a passivating film on the β''-Al_2O_3/molten sodium interface. The modification of this film during the deposition or dissolution of the sodium can be assumed as a cause for the asymmetric behaviour of the internal cell resistance observed.

1. Introduction

One of the most important features that strongly influences the performance of sodium–sulphur cells is their internal resistance and its stability during cycling. The observed increase of the sodium–sulphur battery cell resistance upon cycling is usually considered to be a result of the corrosion of the metal current collector and/or of the container of the sulphur electrode, or of the presence of impurities in the sodium and/or sulphur electrodes [1–5]. It was recently shown that in some cases the increased internal resistance of sodium–sulphur cells is related to the processes which take place on the β''-Al_2O_3/molten sodium interface [6–8]. The asymmetric behaviour of the cells is typical in these cases and manifests itself in the greater d.c. resistance under discharge (anodic dissolution of sodium) than upon charge (cathodic deposition of sodium).

The asymmetric behaviour of the β''-Al_2O_3/molten sodium interface was studied in detail by Breiter *et al.* [9–11] by means of cycling voltammetry, steady state measurements, galvanostatic techniques and impedance measurements in a narrow frequency range (1–10 kHz). The results from these investigations led the authors to the assumption that the asymmetry observed is a result of the existence of a thin passivating interface film of sodium oxide which is electrochemically modified under anodic or cathodic current. The papers of Breiter *et al.* [6–10] also show that the composition of the solid electrolyte most probably determines its ability to form such a thin interface sodium oxide film when it contacts the molten sodium. The mechanism of the asymmetric behaviour rise is not known as yet and its elucidation requires that additional studies be carried out in this field.

Asymmetric behaviour of the sodium–sulphur cell resistance similar to that described by other authors has also been observed in some cases in our experiments. In this paper the results of a.c.

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impedance measurements in a large frequency range (0.01 Hz $\leqslant f \leqslant 10^4$ Hz) on laboratory-scale sodium–sulphur cells with symmetric and asymmetric behaviour are presented.

2. Experimental details

Experiments were carried out on laboratory sodium–sulphur cells of 2 Ah capacity with a central sodium electrode at 320° C. The sodium half-element consisted of a closed-end tube of β''-Al_2O_3 (external diameter 0.92 cm, wall thickness 0.12 cm) which was sealed to the glass–ceramic reservoir for sodium by means of a glass resistant to the action of the molten sodium and sodium polysulphides [12]. The active surface area of the solid electrolyte in contact with sodium was 6 cm^2. A Kovar alloy wire was used as a current collector. Prior to incorporation in the cell the internal volume of the sodium half-element had been evacuated and filled with sodium by means of electrolysis in molten sodium trisulphide in a dry box (DRI-TRAIN MO 40-2 and NI-TRAIN NI 40-2, Vacuum/Atmospheres Co., USA) filled with argon: water vapour and oxygen concentration was lower than 10 p.p.m. The sulphur electrode, 0.7 cm thick, consisted of a graphite felt with about 90% porosity, impregnated with molten sulphur and inserted in a container of a chromium-plated stainless steel used also as a current collector. The β''-Al_2O_3 membranes used (nominal composition 8.9 wt % sodium oxide, 0.75 wt % lithium oxide, balance Al_2O_3 and β-phase content below 5 wt %) were formed by means of isostatic pressing. Subsequently they were fired using a two-step continuous sintering schedule at temperatures of 1620 and 1590° C for 4 and 10 min respectively. Details concerning the preparation of the solid electrolyte membranes are given in [13].

The a.c. impedance measurements were performed using the impedance facility [14] schematically presented in Fig. 1. The Transfer function analyser (TFA), Solartron 1174, performed the correlation and transferred the data via an IEEE 488 interface to the graphics microcomputer, Tektronix 4051. The computer programmed the experiment, received the measurement data (*Re*, *Im* and *f*) for each frequency in online mode and provided storage and processing of the experimental data. The power features of the TFA were expanded by a home-made galvanostat covering a frequency range up to 10 kHz. The instrument had two differential amplifiers (DDA) which amplified the signals for the cell current and voltage and provided a high precision of measurement. The galvanostat operated in the range −1 to +1 A and performed automatic cycling of the cell. The amplitude of the perturbating a.c. current was 5 mA.

The software of the system developed for the impedance study included the following program packs: dynamic programming and control of the experiment; monitoring of the experimental results; data acquisition and file manipu-

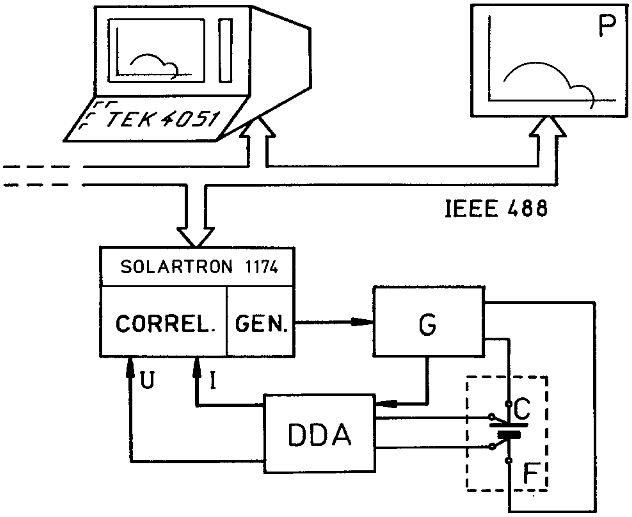

Fig. 1. Diagram of the experimental arrangement for the a.c. impedance measurements of sodium–sulphur cells. TEK 4051, microcomputer; P, plotter; G, galvanostat; DDA, double differential amplifier; C, sodium–sulphur cell; F, furnace.

lation; plotting and printing of the results; and preprocessing and analysis of the impedance data.

The measurements on the high-temperature sodium–sulphur cells involved difficulties due to the operation of the cells under thermostatic conditions, i.e. in a thermostated furnace which was not close to the measurement facility. The inductance of the connecting cables led to significant errors especially at frequencies above 1 kHz. The analysis of the experimental errors [15, 16] showed that the inductance error had an additive behaviour which made correction possible. The experimental results presented in the paper are corrected from the errors of the inductance and the distributed parameters of the equivalent long line of the four-point measurement circuit.

3. Results

The experimental current–voltage relationships for laboratory scale sodium–sulphur cells with typical symmetric and asymmetric behaviour of their internal resistance are shown in Fig. 2. These relationships were measured in the so-called two-phase region (Na_2S_5 + S) at about 40% degree of discharge using the following polarization routine: the cells were kept under open circuit before applying the charge or discharge current for about 15 min. After current switch-on, the cell voltage was measured after 1, 15 and 30 min. The polarization data (Fig. 2) are in qualitative accordance with those obtained by other authors [7] and show the following specific features of the asymmetric cells: (a) asymmetric cells have a greater d.c. resistance at discharge than at charge; (b) the d.c. resistance of the asymmetric cells is greater than that of the symmetric one both at charge and discharge; (c) at discharge with relatively high current densities (above 10 mA cm^{-2}) the polarization of the asymmetric cells slowly decreases with the time after current switch-on. As can be seen from Fig. 2 such a time dependence of the polarization is hardly observed during charge of the asymmetric cells and it does not exist for the symmetric cells at all.

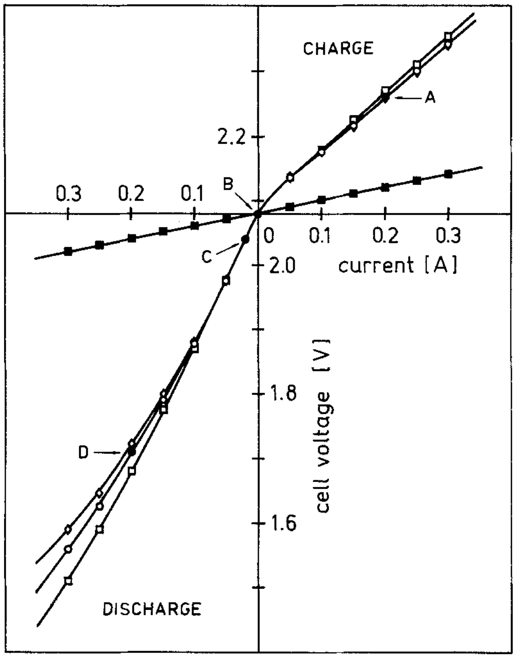

Fig. 2. Current–voltage dependences obtained in the 'two-phase' region for typical sodium–sulphur cells with symmetric (■) and asymmetric (□, after 1 min; ○, after 15 min; ◊, after 30 min) resistance behaviour.

The impedance of the symmetric and asymmetric sodium–sulphur cells was measured at different values of the charge or discharge current 15 min after switching on the current (d.c.). The impedance spectra obtained are presented in Figs 3–6. The corresponding points on the polarization curve at which the impedance spectra were measured are marked in Fig. 2.

In accordance with the observations of other authors [17] the impedance of the symmetric sodium–sulphur cells displays only resistive behaviour over the whole frequency range (0.01–10^4 Hz) and its value is a constant within the limits of experimental error for all charge and discharge currents. The impedance shows dispersion only around the value of the d.c. resistance corresponding to the polarization dependence shown in Fig. 2.

In contrast to the symmetric cells the impedance spectra of the asymmetric cells are considerably more complicated and their shape strongly depends on the operating point on the polarization curve.

In the charge region the impedance spectra of the asymmetric cells (Fig. 3) show a small capacitive loop with a characteristic frequency of about 200 Hz. At $I_{d.c.}$ = 0 (open circuit) the

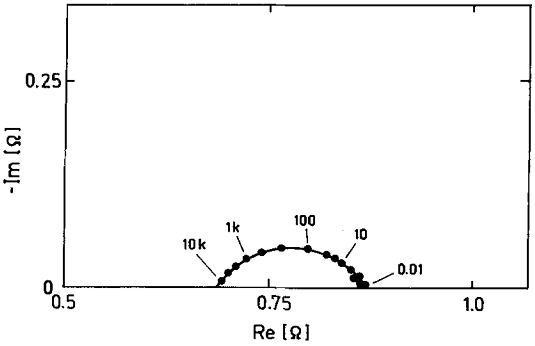

Fig. 3. Impedance spectrum of a sodium–sulphur cell with asymmetric resistance behaviour. (Measured at point A on Fig. 2; frequency marks in Hz; $I_{d.c.}$ (charge) = 0.2 A.)

impedance spectrum (Fig. 4) can be considered as composed of two partially overlapping capacitive loops with characteristic frequencies of about 7 kHz and 200 Hz respectively. The impedance spectrum obtained at relatively low discharge current can be treated in the same way (Fig. 5). At higher discharge currents an additional inductive loop appears in the impedance spectrum (Fig. 6), for frequencies below 10 Hz. It should be noted that at such high discharge currents the cell impedance changes slowly with time (in accordance with the time dependence of the polarization in Fig. 2). In Fig. 6 the experimental data are presented only for the frequency range 0.1–10^4 Hz, because under these conditions the time necessary for measurement in this frequency range is only about 5 min and the influence of the polarization time dependence on the impedance spectrum is avoided. The study of the impedance change with time including the frequencies below 0.1 Hz will be published later.

4. Discussion

The results from the impedance measurements of the sodium–sulphur cells with symmetric d.c. resistance behaviour show that within the limits of experimental error the a.c. impedance of these cells in the frequency range 0.01–10^4 Hz can be considered as composed only of ohmic resistance, corresponding to the bulk resistance of the solid electrolyte. This shows that the polarization of the sulphur electrode and the interface polarizations of the symmetric sodium–sulphur cells are negligibly small.

The results from the impedance measurements of the cells with asymmetric d.c. resistance behaviour clearly show an asymmetric behaviour of the a.c. impedance spectra as well (see Figs 3–6). Only the resistance R_∞, which can be determined by extrapolation to $f \to \infty$, seems to display symmetric behaviour in these cases. The impedance of the asymmetric cells at $f \to 0$ corresponds to the d.c. resistance determined from the slope of the current–voltage relationship in Fig. 2. Since all the sodium–sulphur cells under study have the same construction the absence of the polarization of the sulphur electrode, established for the symmetric cells, leads to the assumption that the polarization of the asymmetric cells is connected with the interfaces β''-Al_2O_3/molten sodium and/or β''-Al_2O_3/molten sodium polysulphides. The capacity, C_1, corresponding to the high frequency capacitive loop of the impedance spectra in Figs 4–6, can be calculated approximately using the formula $C_1 = (\omega_c R_1)^{-1}$, where R_1 is the diameter of the loop and ω_c is its characteristic frequency ($\omega = 2\pi f$). The calculations give values for C_1 which are relatively low, i.e. in the range

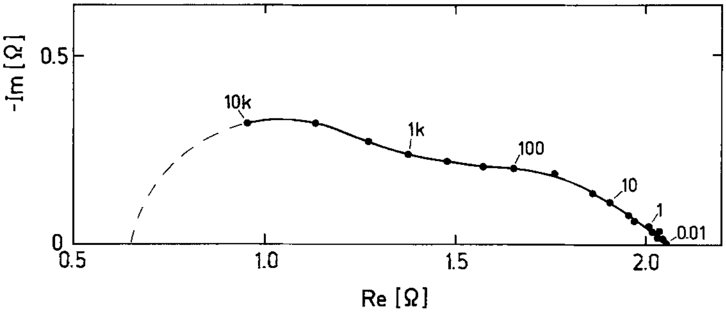

Fig. 4. Impedance spectrum of a sodium–sulphur cell with asymmetric resistance behaviour. (Measured at point B on Fig. 2; frequency marks in Hz; $I_{d.c.}$ = 0 A.)

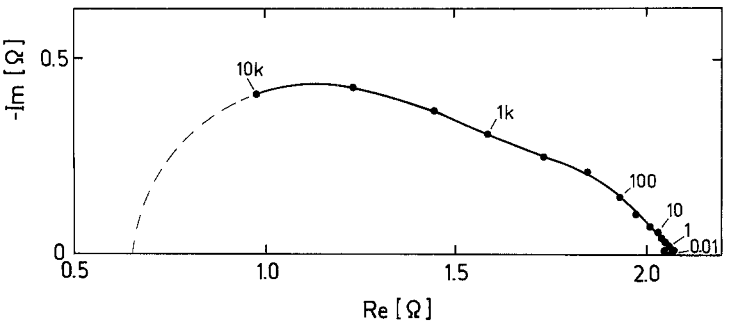

Fig. 5. Impedance spectrum of a sodium–sulphur cell with asymmetric resistance behaviour. (Measured at point C on Fig. 2; frequency marks in Hz; $I_{d.c.}$ (discharge) = 0.02 A.)

2–5 μF cm^{-2}. Similar low values for C_l were also observed by Breiter and Dunn [11] from their study of the asymmetric behaviour of the interface β''-Al_2O_3/molten sodium by means of impedance measurements at relatively high frequency (10^3–10^4 Hz). As was mentioned by these authors the low values of the capacity C_l can not be assigned to the double layer capacity, and it is more reasonable that they are related to the presence of a thin passivating film on the β''-Al_2O_3/molten sodium interface. We also assume that the low values for C_l are due to the existance of such a film. Under this assumption the model suggested by Armstrong and Edmondson [18] may provide a possible means for qualitative interpretation of the experimentally observed impedance spectra of the asymmetric cells. According to this model, neglecting the electrolyte resistance, the total impedance (Z_t) of the metal electrode covered with a continuous passivating film can be presented as a series combination of the film impedance, (Z_f), the metal/film interface impedance, ($Z_{m/f}$), and the film/electrolyte interface impedance, ($Z_{f/e}$). As was noted above, the high-frequency capacitive loop of the experimental impedance spectra can be related to the Z_f. Then the low-frequency part of the impedance spectra will include $Z_{m/f}$ and $Z_{f/e}$. The inductive loop observed in the low-frequency part of the impedance spectrum in Fig. 6 can be explained according to [18] in terms of a relaxation process on the interface film/electrolyte as a result of the exchange of both cations and anions constituting the film. The relaxation time approximately evaluated from the experimental diagram (Fig. 6) is about 1 s. It should be noted that a similar inductive behaviour of the impedance is also predicted from models which include adsorption of inhibitor [19, 20], adsorbed intermediate [21] etc. It is obvious that the qualitative interpretation of the experimentally observed impedance spectra of the present paper is not the only possible one, but it supports the similarity between the phenomenon of asymmetry and the passivation behaviour of the metals in electrolyte solutions. It seems to substantiate the suggestion made by Breiter and Dunn [9–11] that the asymmetric polarization is most probably due to the existance of the passivating film on the β''-Al_2O_3/

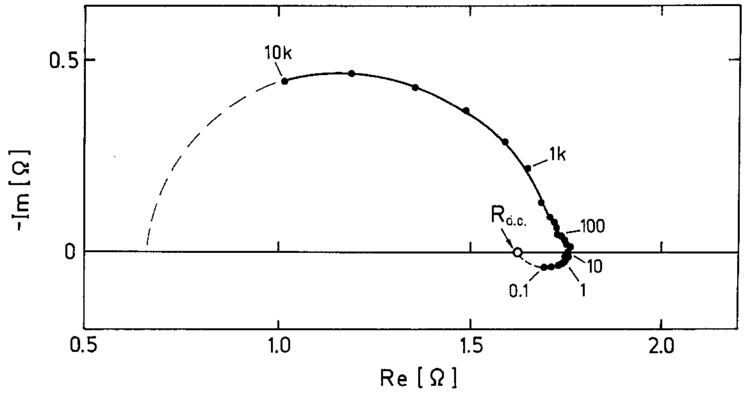

Fig. 6. Impedance spectrum of a sodium–sulphur cell with asymmetric resistance behaviour. (Measured at point D on Fig. 2; frequency marks in Hz; $I_{d.c.}$ (discharge) = 0.2 A.)

molten sodium interface which is modified when anodic or cathodic current flows. The nature of this film as well as the causes of its formation are not yet known and are still under investigation.

Acknowledgement

The authors thank Dr A. Yanakiev and Dr R. Kvachkov for supplying the β''-Al_2O_3 membranes and for their help in assembling the sodium–sulphur cells.

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