

Carbon-air electrode with regenerative short time overload capacity: Part 1. Effect of manganese dioxide

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To increase the overload capacity of the carbon-air electrode in alkaline electrolyte, without seriously changing the electrode potential during short-time overload periods, small amounts of MnO_2 were added to carbon and the effects investigated. The potentiodynamic investigations revealed the existence of two reducible manganese species with reduction potentials of about -280 mV and -400 mV. The second potential corresponds to the known reduction process $\text{Mn(III)} \rightarrow \text{Mn(II)}$ whilst the first one corresponds to a reversible process (the product is easily reoxidized by air or anodically), not reported in literature as yet. It was explained in terms of a new redox potential for the system Mn(III)/Mn(II) , both species being strongly and irreversibly adsorbed at the carbon surface. The galvanostatic discharge curves in the absence of air indicate that a sufficient overload capacity of about 40 C cm^{-2} is available if 22% (wt) MnO_2 is added. Steady-state polarization curves in the presence of air indicate the catalytic effect of small amounts of MnO_2 for the oxygen reduction reaction.

1. Introduction

One of the serious problems in the application of electrochemical power sources in traction is the requirement for some degree of overload capacity for short-time periods during the acceleration of the electric vehicle. In this period the necessary current drain can be 3-5 times larger than that in normal driving periods [1]. Therefore, batteries with extra power capabilities are of general interest for practical applications.

Fuel cells and metal-air battery systems usually operate at current densities determined by the performances of the air electrodes. The principal limiting factor for the air electrode at high current densities is the blocking of the pores with accumulated nitrogen and the insufficient access of oxygen to the reacting zone of the

electrode. To solve this problem in practice, Kordesch used in his electric car a hybrid fuel cell plus lead-acid battery system [2].

The essential idea of this work is to overcome the principal limiting factor for the short-time demand for extra power by introducing a supplementary oxygen source into the normal carbon-air electrode. This source should be able to deliver oxygen during the periods of extra power need, and simultaneously should have regenerative properties so that the reduction products may be reoxidized by air during the normal or lower current drains.

For this purpose the properties of the carbon-air electrodes with the additions of various amounts of manganese dioxide either in the form of crystalline MnO_2 or by impregnation with KMnO_4 solution have been investigated, using the cyclic potentiodynamic or the galvanostatic method.

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2. Experimental

The active carbon powder used in the experiments was GM Type (Miloje Zakić Factory, Kruševac, Yugoslavia), treated as described elsewhere [4, 5], to obtain a surface area higher than $1500 \text{ m}^2 \text{ g}^{-1}$, without any supplementary catalyst impregnation.

Manganese dioxide (reagent grade) was obtained from VEB Berlin-Chemie, Berlin-Adlershof and potassium permanganate (reagent grade) from Laphoma, Skopje, Yugoslavia. The two manganese compounds were ground in a mortar and passed through a $80 \mu\text{m}$ sieve prior to use.

In all experiments the active carbon was used in a mixture with P.T.F.E. emulsion (Du Pont TEF30) in a proportion by weight of 4:1. The manganese dioxide was mechanically mixed with the carbon before the P.T.F.E. addition; the permanganate was dissolved in a portion of P.T.F.E. emulsion prior to mixing the P.T.F.E. with the carbon. After mixing, the samples were dried at room temperature before further use.

In one set of experiments the samples were used just as described above. In another set, sandwich electrodes were pressed from the samples, according to the method described elsewhere [6]. The pressed electrodes, 19.5 mm in diameter, were prepared from 300 mg of polyethylene powder. They incorporated a nickel-plated iron gauze disc with the appropriate connection wire and samples of the carbon P.T.F.E. admixture prepared as described above. For all electrodes 160 mg of carbon were used, and the pressing force was 90 kg cm^{-2} .

Three different experimental half-cell arrangements were used. The first ('powder cell') shown in Fig. 1 is very similar to that of Despić, Dražić and Kadija [7], but made of lucite. The geometric surface of the powder electrode material was 1 cm^2 . For this cell a standard quantity of 65 mg of active carbon powder was used as sample, plus manganese compounds and P.T.F.E. as additives. The quantity of the electrolyte in the cell was 200 ml.

The second type of half-cell arrangement used is shown in Fig. 2 ('small cell') and was made of PVC. In this cell the samples were used in the form of pressed electrodes. It should be empha-

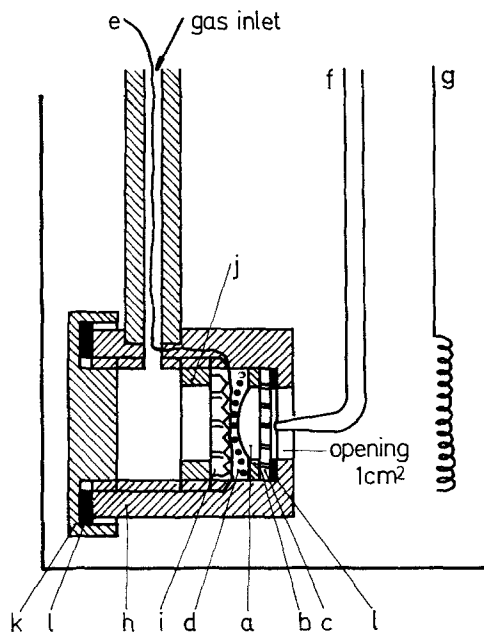


Fig. 1. The powder half-cell arrangement. a, Powder electrode material; b, 0.5 mm thick spacing ring; c, fritted glass disc; d, current collector (platinum gauze); e, connecting wire; f, Luggin capillary; g, nickel counter electrode; h, lucite electrode holder; i, gas distributing plate; j, ring shaped screw; k, closing plate; l, gaskets.

sized that the pressed electrodes had 3 cm^2 of geometrical surface but the electrode surface directly exposed to the electrolyte as well as to the gas was only 1.79 cm^2 , the rest being screened by the gasket. The quantity of electrolyte used in this cell was 4 ml only.

Both these types of half-cells were supplied by gases from the gas purification equipment.

The third half-cell arrangement used was a simple three-electrode cell ('nickel counter electrode') with a pocket-type working electrode holder. The gas supply was the surrounding air. This arrangement was very similar to that described elsewhere [6]. Samples in the form of pressed electrodes were used as in the small cell and the exposed surface area of the sample was the same. The quantity of the electrolyte used in this cell was 200 ml.

All half cell arrangements had thermostatically controlled jackets maintained at 30°C . The electrolyte was aqueous 9 N KOH in all experiments. Potentials throughout are referred to $\text{Hg}|\text{HgO}|9\text{N KOH}$ at room temperature.

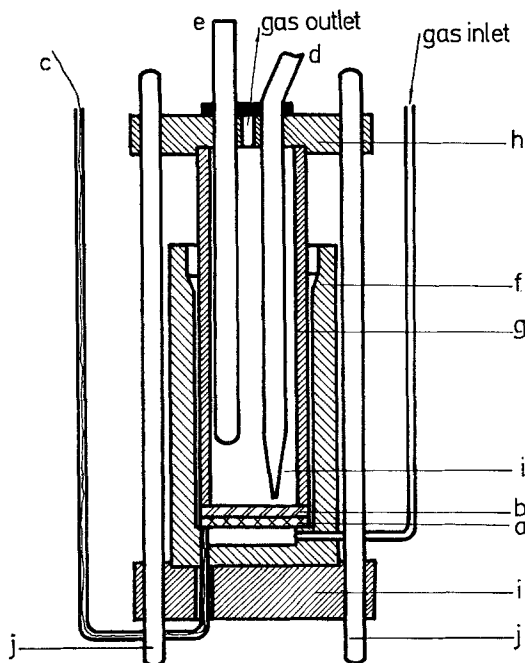


Fig. 2. The small half-cell arrangement for testing pressed electrodes. a, working carbon electrode; b, fritted glass disc; c, wire for connecting the working electrode; d, Luggin capillary; e, graphite counter electrode; f, g and h, PVC cell parts; i, electrolyte compartment; j, clamping screws.

The measurements in the powder cell, on samples not pressed, were carried out by the potentiodynamic method, at slow sweep rates (20 mV min^{-1}). The measurements in the small cell, on pressed electrodes, were carried out galvanostatically at currents expressed in C units calculated relative to the quantity of manganese in the samples*.

For measurements carried out in the powder cell and the small cell the following electronic equipment was used: a Wenking 61 RH potentiostat driven (only for potentiodynamic measurements) with a Hewlett Packard function generator Type 3310A, a Hewlett Packard DC Vacuum tube V-meter Model 412A and a Hewlett Packard X-Y recorder Type 7000 AM.

In the third half-cell arrangement the steady-state current versus potential characteristics of electrodes supplied with air were measured. The electrode was polarized cathodically by means of an external d.c. device at different current

* 1 C corresponds to the necessary current for 1 h discharge rate of the existing electrochemically active material (in this case MnO_2).

densities, while the electrode potentials were measured with respect to the reference electrode and Luggin capillary.

3. Results

3.1 Potentiodynamic measurements

In order to investigate the reversibility of the electrochemical reduction and oxidation, and reoxidation by the air of the cathodically reduced material, the cyclic potentiodynamic current/potential characteristics were measured for powder (unpressed) samples in air-free electrolyte.

The chosen potential range was between 0 and -750 mV . A new sample was first exposed to air (very slow bubbling) for $\frac{1}{2} \text{ h}$ and then for 1 h to argon to remove oxygen from the pores. The slow cathodic sweep (20 mV min^{-1}) was started and the current/potential characteristics recorded. Throughout the measurement argon was slowly bubbling through the electrode. No correction was made for IR drop.

Since permanganate is reduced by carbon mostly to MnO_2 [10, 12], it seemed most appropriate to express the amounts of permanganate added by the equivalent amounts of MnO_2 , even though small amounts of lower valency manganese compounds might be formed. Characteristics recorded during the first one and a half potential cycles are presented in Fig. 3a for a sample containing 7% MnO_2 introduced via permanganate.

Characteristics for a carbon sample without MnO_2 added are presented in Fig. 3b for comparison. They can be considered as the background in the recordings for the electrodes with added MnO_2 . The successive curves recorded during the following cycles are not identical but have a very similar shape. The comparison between Fig. 3a and 3b allows one to separate the manganese cathodic and anodic peaks by the tangential lines as shown in Fig. 3a. The positions of these peaks are reproducible; the areas under the peaks are also reproducible ($\pm 2\%$) for the two cathodic peaks and one anodic peak presented in Fig. 3a. The area under the peaks corresponds to the 70% of the charge needed assuming a one electron redox reaction

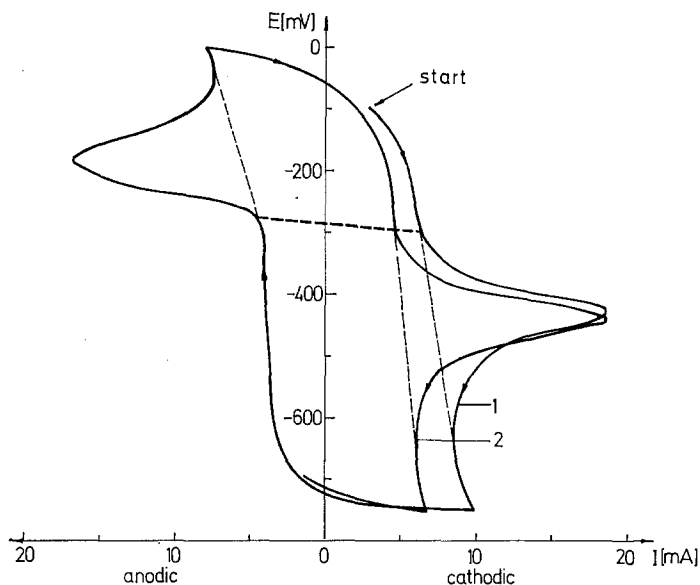


Fig. 3. (a) The cyclic potentiodynamic curves for a carbon electrode with 7% MnO_2 introduced via permanganate: 1-first cycle; 2-second cycle.

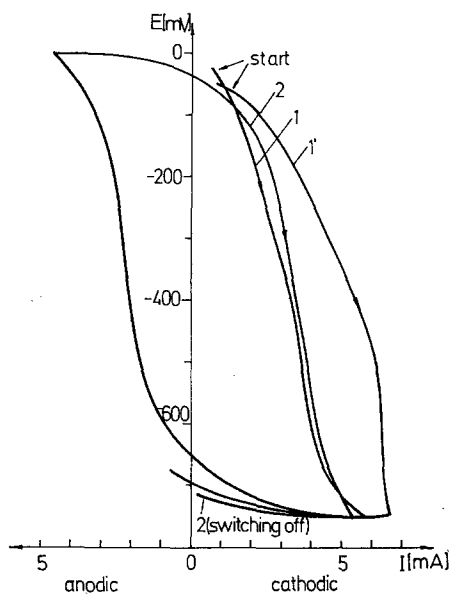


Fig. 3. (b) The same as 3a but for a sample without manganese additive. 1-first cycle; 2-second cycle; 1'-after air regeneration.

for the manganese in the sample. The reversible redox potential is about -280 mV.

The characteristics of a similar sample after

many hours of potentiodynamic cycling in the specified potential range are shown in Fig. 4. The areas under the anodic and under the cathodic peaks (curve 1) are reduced to one half by comparison with Fig. 3a but the positions of the peaks are the same and the redox potential is about -280 mV as before. In this diagram the cathodic characteristics after the supplementary passing of air through the electrode (i.e. air regeneration) of the cathodically reduced sample are also presented (curve 1). After recording the curve 1 the current was switched off at the point when reduction of the sample was maximal (as indicated on the figure) and air was bubbled through the sample for 3 h. Argon was then passed through the sample for 1 h and the characteristics measured as described for the original sample. By the same method the characteristic for a sample without manganese presented in Fig. 3b, curve 1', was measured. One can observe that the characteristic manganese peak reappears after air regeneration, in the same way as after anodic reoxidation. The area under the peak on curve 1' in Fig. 4 is the same as for curve 1 in Fig. 3b.

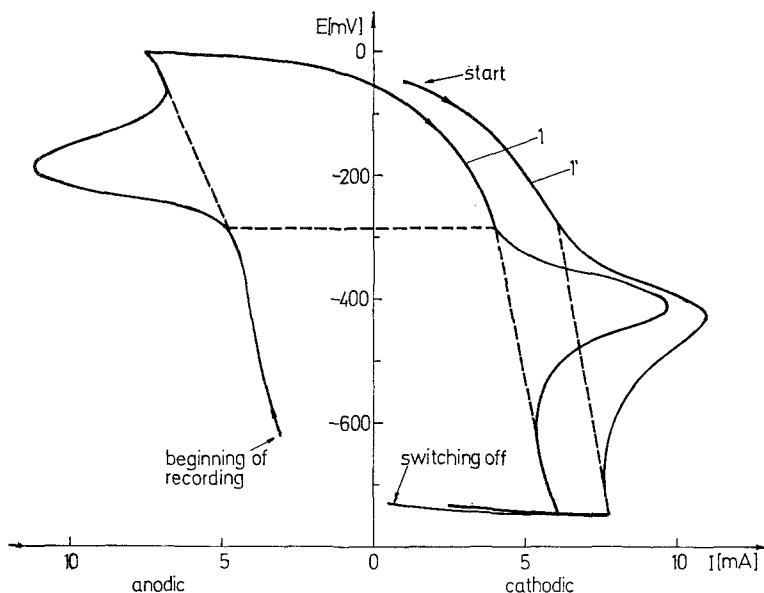


Fig. 4. The cyclic potentiodynamic curves for the same electrode as in Fig. 3a: 1-after longtime cycling; 1'-after air regeneration.

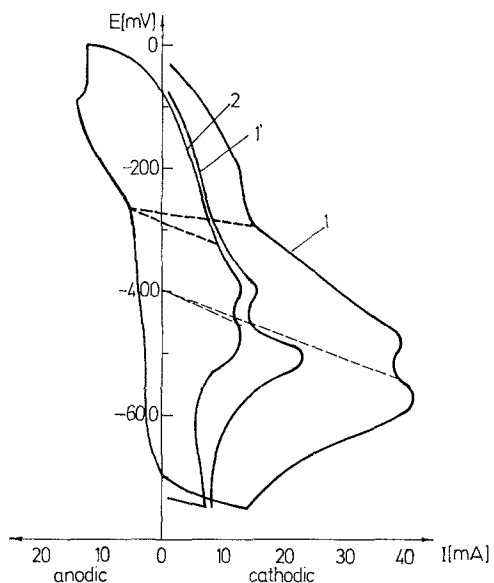


Fig. 5. (a). The cyclic potentiodynamic curves for a sample containing 22% of MnO_2 introduced via permanganate: 1-first cycle; 2-second cycle; 1'-cycle after the additional 1 h air regeneration.

Figs. 5a and 5b present similar curves for new samples which contain larger quantities of manganese, introduced in the form of permanganate or manganese dioxide powder, respectively. When manganese was added in the form

of permanganate two distinct peaks were observed on all cathodic curves. The first peak can be identified as that seen when the small quantity of manganese was introduced as permanganate (Figs. 3 and 4). The second cathodic peak appearing at a more negative potential was absent previously. Its potential can be estimated as about -400 mV. During the first cathodic reduction of the sample prepared with manganese dioxide powder addition (curve 1 on Fig. 5b) the first peak is absent; it appears after the first reduction and anodic reoxidation cycle (this curve is not presented) and after air regeneration of the cathodically reduced sample (curve 1'). Another essential difference between Figs. 5a and 5b can be observed. From Fig. 5b it is clear that a great part of the material was not reduced completely during the cathodic potential sweep because after changing the direction of the sweep to anodic, the current remains cathodic up to a potential close to -400 mV (curve 1). In both figures the differences between the first and second cathodic discharges can be observed. The charge drawn during the first reduction is much larger than in the following ones. It was additionally observed that during the experiments with samples containing large quantities of manganese the fritted glass displaced between

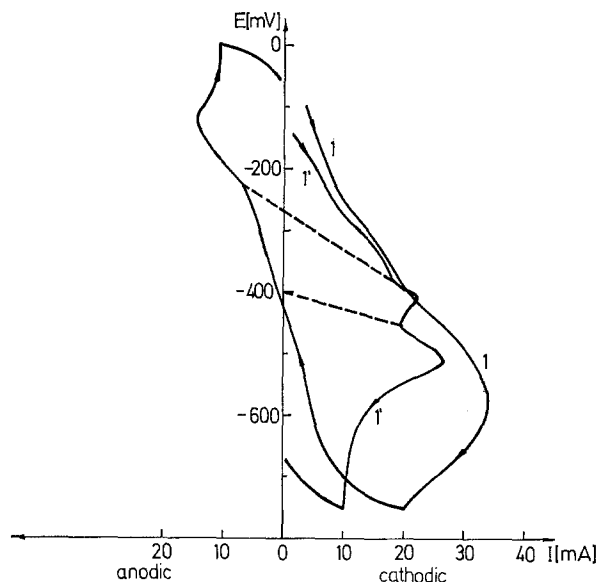


Fig. 5. (b) the same as Fig. 5a but for a sample with 40% of MnO_2 introduced as MnO_2 powder: 1-first cycle; 1'-after air regeneration.

the sample and the electrolyte was intensely violet-brown coloured. It appears that some material is washed out from the sample during the reduction and reoxidation cycles.

3.2 Galvanostatic measurements

As mentioned before, galvanostatic measurements were carried out on the pressed samples in the 'small cell'. They were carried out at currents expressed in C units calculated relative to the quantity of manganese compound introduced originally into the sample assuming a two-electron reaction: $\text{Mn(IV)} \rightarrow \text{Mn(II)}$. The new sample was mounted into the cell with the electrode in the electrolyte overnight prior to the measurement. Before the measurement, firstly air and then argon were very slowly bubbled through the electrode for $\frac{1}{2}$ h in each case. Then the potential versus time characteristics at a chosen current drain was recorded, with argon bubbling through the cell. At the chosen potential limit (-800 to -900 mV) the current was switched off and the sudden change of potential recorded. This potential change was taken as the IR polarization, and used for IR correction of the recorded curves; this problem will be discussed in more detail later.

Subsequently air was passed through the electrode for a definite time, then argon for $\frac{1}{2}$ h and the measurement repeated at the same current drain as before. The procedure was repeated several times but with different duration of air regeneration. Usually the characteristics were recorded for a freshly prepared electrode (curves O), then after the first (1 h) air regeneration, the second (1 h) regeneration, the third ($\frac{1}{2}$ h) regeneration and the fourth ($\frac{1}{4}$ h) air regeneration (respectively curves I, II, III and IV); for several samples additional characteristics after the supplementary fifth (1 h) air regeneration were also recorded (curves V).

The analogous characteristics were recorded for the carbon electrodes without any manganese addition at the same currents as for the samples with manganese. An example of such a characteristic for a pure carbon electrode is shown in Fig. 6 (broken lines); for the sake of clarity only limiting curves are presented.

Fig. 7 represents an example of the complete characteristics for an electrode with 22% of MnO_2 introduced via permanganate, corrected for the IR drop and the background carbon capacity, measured at the $\frac{1}{2}$ h discharge rate (i.e. 2 C) relative to the quantity of manganese originally introduced (calculated for $\text{Mn(IV)} \rightarrow$

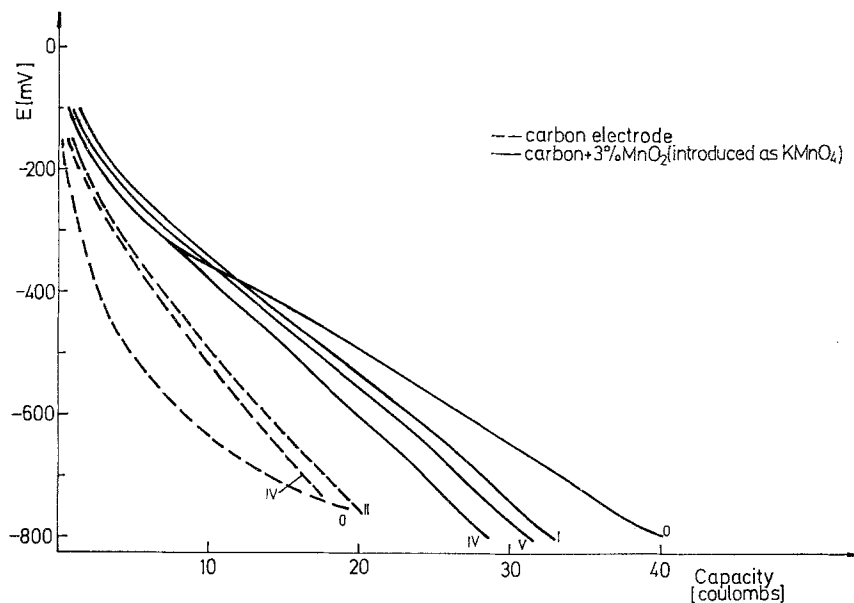


Fig. 6. Galvanostatic discharge curves of pure carbon and carbon with 3% MnO_2 added. The figures indicate the number of air regenerations. $I = 21.6$ mA. IR drops corrected.

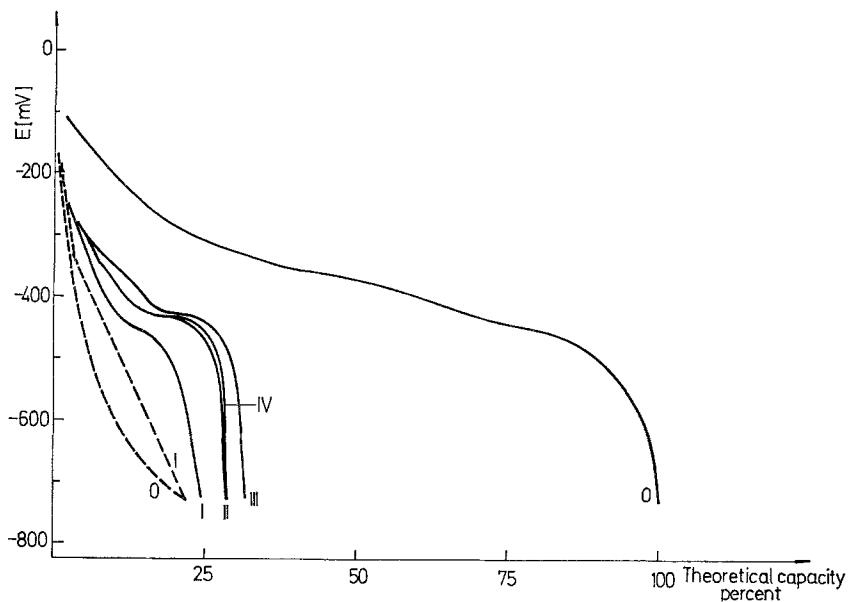


Fig. 7. Galvanostatic discharge curves at 2 C rate for electrode with 22% MnO_2 introduced via KMnO_4 . Broken lines—pure carbon background. Full lines— MnO_2 capacities (total minus background).

Mn(II) reaction). For comparison, the pure carbon electrode background is also presented (broken lines).

For comparison, characteristics for the first discharge of the electrodes differing in the quan-

tity of MnO_2 and discharged at different discharge rates are presented in Figs. 8a and 8b.

The curves measured after successive air regenerations were not as presented in Fig. 7 for all the samples but the electrode discharge

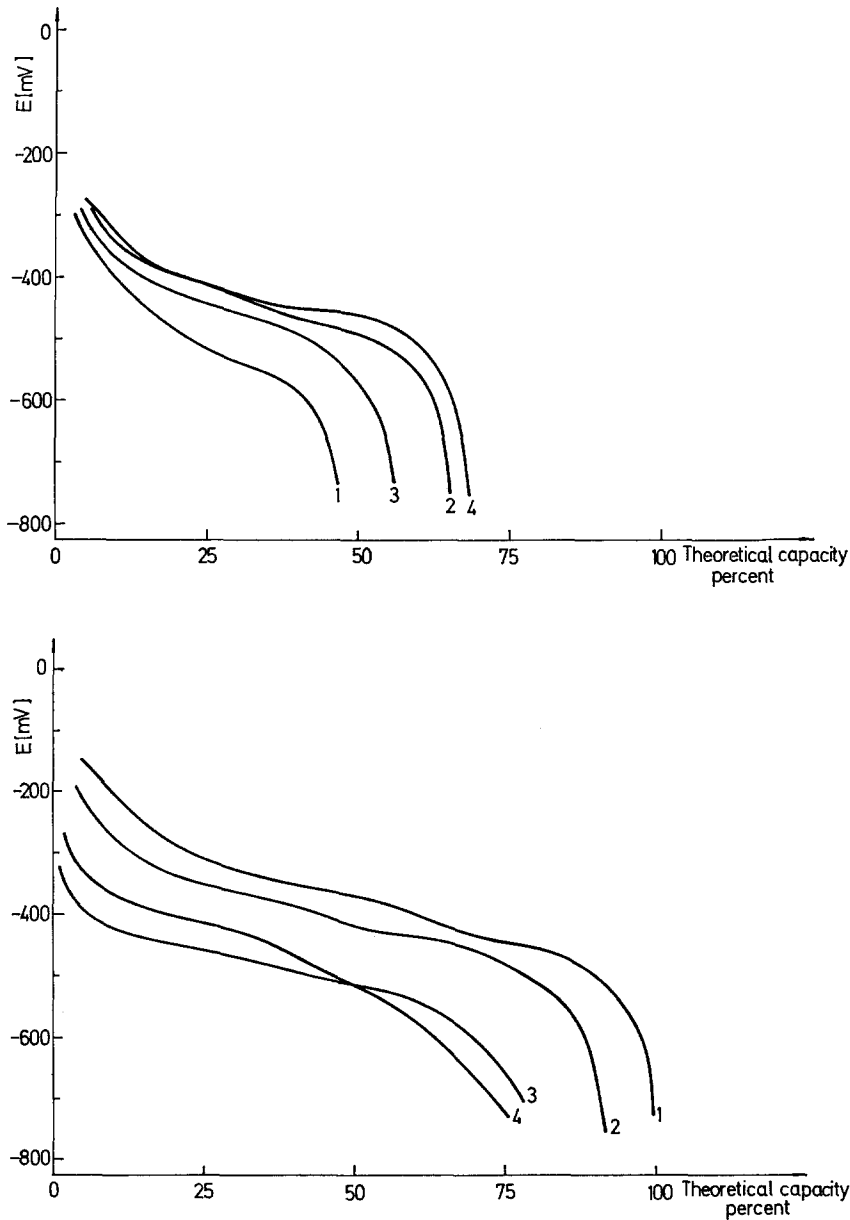


Fig. 8. First galvanostatic discharge curves at different discharge rates for electrodes with MnO_2 introduced: (a) as MnO_2 powder; (b) as KMnO_4 . Curve 1—22% MnO_2 at 2 C rate; curve 2—22% at 1 C rate; curve 3—44% MnO_2 at 1 C rate; curve 4—44% MnO_2 at 1/2 C rate.

capacity after air regeneration was in all cases nearly 25% of that measured for the fresh electrode. All the curves for fresh (O) and air regenerated electrodes (I-IV) had two more or less distinct plateaux, the first at a potential of about -350 mV and the second usually longer than the first at potentials lower than -400 mV.

The succession of initial discharge curves presented in Figs. 8a and 8b is very characteristic. The curves for the electrodes containing manganese dioxide are just the opposite of those prepared using permanganate solution. The highest relative discharge capacity was obtained for the electrode prepared with the lower

permanganate content, at the highest discharge rate. Taking into account that air regeneration gives in any case nearly 25% of the originally measured relative capacity, air regeneration also gives the best results for this sample.

There is another essential difference between the electrodes prepared with the manganese dioxide powder and the permanganate. For samples prepared with manganese dioxide powder the capacity when discharged at potentials more positive than -400 mV never exceeds 20% of the total theoretical capacity, but for electrodes prepared with low permanganate content it can attain values of 50 or even 75%.

The ohmic resistance calculated from the IR drop was lowest for the electrodes without manganese additions (nearly 1.5Ω); in this case it was constant during the measurement. Similar and almost constant ohmic resistances were measured during the experiments with the lowest, 3% manganese dioxide addition, which will be described later. For all the other samples the ohmic resistance was higher and increased for successive curves. The highest increase was observed during the recording of the first two curves. The resistance measured after the initial discharge of the fresh electrode was much higher than that for the electrode without manganese and the resistance measured after the discharge of the electrode regenerated by air for the first time (curve I) was much higher than that after curve O. Further changes were negligible.

For electrodes prepared with manganese introduced in the form of permanganate, the ohmic resistance increased with increasing quantity of manganese and decreasing discharge rate. It increased to nearly 15% of the initial value for the sample represented by curve 4 in Fig. 8b. Electrodes prepared with the highest manganese dioxide content discharged at the lowest rate and had the lowest resistance (curve 4 in Fig. 8a).

One additional observation was made during the experiments. After each experiment the fritted glass disc was characteristically coloured. It was violet from the side adjacent to the electrode and brown from the opposite side. The electrolyte in the electrolyte compartment of the cell was also slightly brown-coloured and it contained two different precipitates: a brown

colloidal one and a black powder, probably some manganese (III) oxyhydroxide and manganese (II) hydroxides, and manganese dioxide respectively.

A standard galvanostatic measurement was also made for the electrodes containing a very small (3%) quantity of manganese dioxide introduced into carbon via permanganate. This quantity of manganese dioxide which is probably irreversibly adsorbed on the carbon was recalculated from the measurement presented in Fig. 4. The characteristic curves for this manganese content are presented in Fig. 6 (full lines). The background correction could not be made because the measured capacity of the electrode was not much greater than the background capacity of carbon. It was evident that the sample had distinctly greater capacity than the pure carbon electrode and that this capacity was easily and reproducibly restored by air regeneration up to approximately 70% of the originally measured value. It should be emphasized that the discharge rate in this experiment, recalculated on the basis of the quantity of manganese present, was extremely high, being nearly $10 C (1/10 h)$. In this experiment neither the formation of precipitates in the electrolyte nor the colouration of the fritted glass disc was observed. The IR drop was the same as that for the electrodes without manganese.

3.3 Steady-state potential-current characteristics

The steady-state potential-current characteristics of the pressed carbon electrodes in air were measured to see the effect of manganese dioxide additions on this essential characteristic of the carbon-air electrode from the practical point of view.

The results of these measurements are summarized in Fig. 9. The introduction of a large quantity of manganese via permanganate caused drastic deterioration in the performance of the electrode. The introduction of the same quantity of manganese in the form of dioxide powder had a much smaller effect. The addition of moderate quantities of manganese dioxide powder gave a beneficial effect in the region of high currents. The addition of a very small quantity of manganese in the form of permanganate appreciably

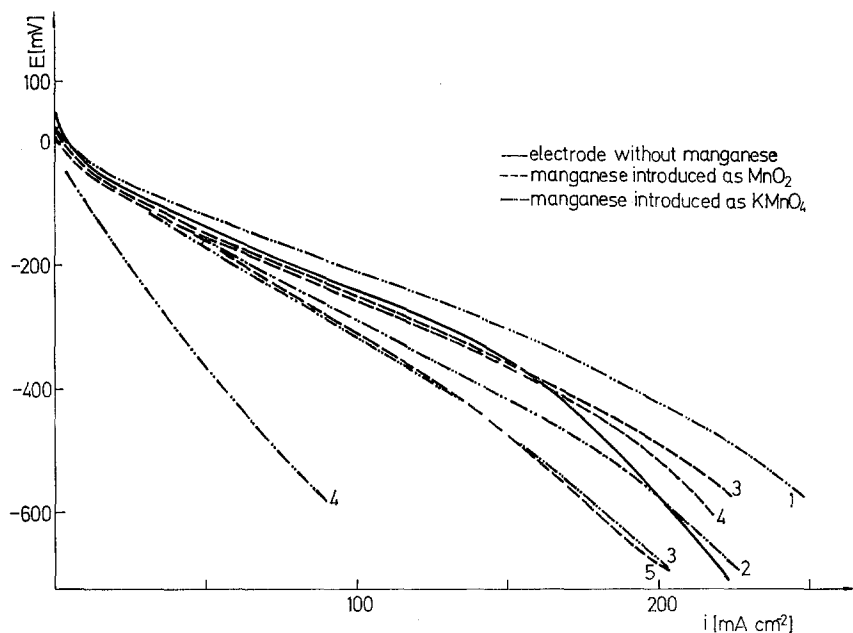


Fig. 9. Stationary polarization curves for carbon-air electrodes without and with different amounts of MnO_2 introduced as MnO_2 or KMnO_4 . 1. 2.5%; 2. 4.5%; 3. 9%; 4. 22%; 5. 44%.

lowered the electrode polarization over the whole current density range.

During the experiments with high contents of manganese introduced via permanganate, washing out of a colloidal brown material into the electrolyte was observed.

4. Discussion

The theory of the manganese dioxide cathode discharge in concentrated alkaline electrolyte is still rather a controversial problem [3], but the most widely accepted discharge scheme is that of Kozawa and Yeager [8]. Typical galvanostatic discharge curves are presented in Fig. 10. The first reduction step is the reduction of manganese (IV) to manganese (III); this process is accompanied by the continuous decrease of electrode potential down to about -400 mV. The reaction may proceed by an electron-proton mechanism in the homogeneous phase [9]. Several authors have observed a violet colouration of the paper separator enveloping the cathode during the discharge, cementation and hardening of the sample during this discharge stage [8, 10]. The colouring was explained as the washing out of

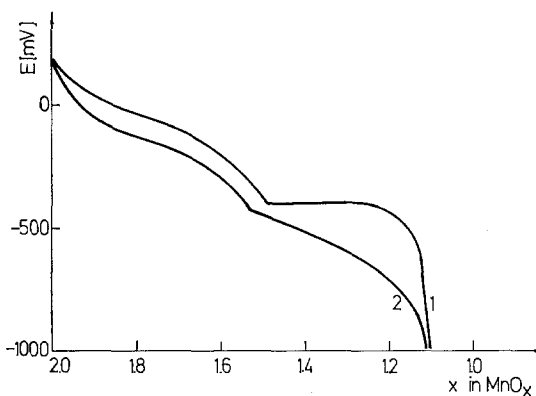


Fig. 10. Typical galvanostatic discharge curves for MnO_2 (after Kozawa and Yeager [8]). 1. At low current; 2. At currents 30 times larger.

manganese (III) ions from the bulk of the manganese dioxide phase.

The second reduction step, represented by a large plateau on the galvanostatic discharge curve, is for the reduction of manganese (III) to manganese (II). This process proceeds at a constant potential of -400 mV, and it is a heterogeneous reaction according to the thermodynamic theory of Vetter [11]. The solubilities of Mn(III) and Mn(II) ions in 9N KOH are

significant ($\sim 10^{-3}$ M), so that at low discharge rates the reduction potential is governed by the Nernst equation. The potential is stable as long as the two solid phases supply ions to the solution. The plateau potential at -400 mV has been verified as the Mn(III)/Mn(II) redox potential by polarographic measurements [8].

All the previous investigations on the cathodic reduction of manganese dioxide were carried out on pressed samples with small additions of graphite or carbon black, or on samples of manganese dioxide anodically deposited on graphite rods. In our experiments the proportion of manganese dioxide to carbon was very small and active carbon having a very large surface area was used. As can be seen in Fig. 3a, for the lowest manganese to carbon ratio we observed a much higher reversible redox potential than that normally observed (-400 mV). This potential can be estimated as -280 mV. For higher quantities of manganese dioxide introduced via permanganate solution into the active carbon, two distinct peaks were observed on the potentiodynamic cathodic curves (Fig. 5a). The first is the same as that observed for low manganese content and the second can be extrapolated to zero current at -400 mV. The shape of the first discharge curve measured for the sample prepared with manganese dioxide powder (Fig. 5b) could be estimated from the galvanostatic discharge curve presented in Fig. 10. After the reoxidation of such a reduced electrode, the new peak, at the higher redox potential, also appears. It should be specially emphasized that the redox potential of -280 mV is the reversible potential for a rather fast reversible process; the cathodic as well as the anodic polarizations are very small.

To explain the appearance of the -280 mV redox potential, for which we did not find any reference in the literature, one must take into account the great surface area of the active carbon substrate in our samples. The reduction of permanganate to manganese dioxide by organic substances is a known process [10, 12]. It can be expected that the mixing of the permanganate solution with the active carbon results in the reduction of permanganate and in the extremely fine distribution of the manganese (IV) compound (and perhaps manganese (III)

and also manganese (II)) on the carbon surface. Adsorption of the manganese compound thus obtained on the active carbon is also known. Daniel-Bek and co-workers [12] observed that when up to about 3% of permanganate is introduced into the active carbon, the manganese cannot be washed out from the carbon, i.e. it is adsorbed irreversibly. The same quantity of adsorbed manganese can be calculated from our measurements (Fig. 4) considering a one-electron redox reaction.

Our observations can be explained assuming the existence of two forms of the Mn(III)/Mn(II) couple: the well-known form with redox potential -400 mV and a new, more active form, with the reversible redox potential -280 mV. If both Mn(III) and Mn(II) are strongly adsorbed at the surface, their free energy states are changed by the amounts equivalent to their free energies of adsorption. Hence, the more positive redox potential can be interpreted as that for the two strongly and irreversibly adsorbed manganese species at the carbon surface. The potential difference between the plateaux at -400 mV and -280 mV is caused by the effective differences in the free energies of adsorption for the two species ($\Delta\Delta G_{\text{ads}} = -zF\Delta E = 1 \times 96500 \times 0.12 / 4.18 = 2750$ cal mole $^{-1}$). The close proximity of the active carbon surface to MnO $_2$ crystallites may even provoke the change of some part of the normal manganese compound into a more active form if any transport of manganese ions is possible (compare curve 1 with curves 3 and 1' on Fig. 5b). It is possible that the 'activation' of carbon rod electrodes with KMnO $_4$ when used as the indicator electrode for potentiometric titration [13], which has up to now not been explained, may be due to the formation of the above adsorbed redox couple.

Nearly all the investigations on the cathodic reduction of manganese dioxide reported in the literature were carried out at relatively low 'current densities' expressed in terms of current per gram of MnO $_2$ (0.5–60 mA g $^{-1}$ MnO $_2$). At higher 'current densities' no plateaux were observed (Fig. 10). Currents used in our experiments, recalculated as 'current densities' on the manganese compound originally introduced into the samples were in the region of 600–1200 mA g $^{-1}$ and even higher in some cases. From this

point of view one can expect high discharge polarizations. The shape and the succession of discharge curves for samples prepared with manganese dioxide powder (Fig. 8a) are understandable. Similarly it explains the low potential levels of plateaux on some of our other diagrams. For an explanation of the shape and the succession of discharge curves of samples to which manganese dioxide was introduced via permanganate solution (Fig. 8b) one must take into account the existence of the manganese dioxide in the postulated more active form and the additional slight solubility of manganese (III) and manganese (II) ions in the electrolyte. When an electrode containing a great quantity of highly dispersed manganese (IV) compound is reduced at a relatively low rate, the probability of washing out the soluble manganese (III) reduction by-product from the electrode is relatively high. The probability of Mn(III) ions being washed out is less when the manganese-to-carbon ratio is low and when the discharge rate is high. The washing out of manganese ions during our experiments was shown by the colouration of the fritted glass disc and by the appearance of precipitates in the electrolyte compartment. This washing out was responsible too for the rise of the IR polarization during the experiments because of the reprecipitation and plugging of the pores in the fritted glass disc.

It was demonstrated that reduced electrodes can be regenerated to a large extent by air. The results presented in Fig. 4 indicate that air re-oxidation of adsorbed manganese (II) ions to manganese (III) ions can be complete. The air regeneration of electrodes discharged galvanostatically restored nearly 25% of the original capacity. It is evident that during the high current discharge of a thick electrode the reduction process proceeds in different regions of the electrode at different rates. Mass transport processes must be involved here and also during regeneration. The reduction product and by-product have considerable solubilities in the electrolyte. In our experiments the washing out of soluble products was forced to some extent by the gas flowing through the electrode; the gasflow was not carefully controlled and it could be the principal reason for the rather poor reproducibility and decay of capacity in successive regenerations.

The good reproducibility and very high degree of air regeneration was obtained for the sample with a very low quantity of manganese dioxide (Fig. 6). One has to remember that the first reduction takes place in the whole volume of the electrode having 3 cm² of geometric surface, while for the air regeneration the parts of the electrode covered with gaskets are not probably accessible to air. Hence, only 70% of the electrode surface and volume is easily accessible for the regeneration process.

The last very important practical point concerning the use of carbon-air electrodes with added manganese dioxide is the effect of the latter on the stationary characteristics of the carbon-air electrode (Fig. 9). The large quantity of additive causes a drastic degradation of the air performance of the electrode, probably because of the plugging of the transport pores and perhaps by some blocking of active centres on the carbon surface. Moderate additions, especially in the form of manganese dioxide powder, improve the steady-state characteristics only in the region of high current density. It might be assumed that this is the result of the formation of new pores after the washing out of manganese dioxide particles, i.e. increase of the porosity. This cannot be the correct explanation for the beneficial effect of the very small additions of manganese (equivalent to nearly 2.5% MnO₂) introduced via permanganate solution, on the steady-state characteristics of the electrode in air, over the whole range of current densities. The adsorbed manganese ions are known to be good catalysts for the decomposition of hydrogen peroxide on the active carbon surface [12]. This may well explain the beneficial influence of the small quantity of manganese in the carbon on the whole steady-state performance of the carbon-air electrode.

5. Conclusions

Three essential conclusions can be drawn from the present investigation:

1. The manganese (III)/manganese (II) ions reversible redox potential is changed in the presence of the active carbon surface from -400 mV to -280 mV.

2. The presence of some manganese ions in the active carbon electrode considerably increases the carbon cathode capacity; this supplementary capacity can be restored by the action of air.
3. The introduction of a small quantity of manganese ions into the standard carbon-air electrode considerably improves the performance of the electrode.

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