Evaluation of the Porosity and the Nano-structure Morphology of MnO$_2$ Prepared by Pulse Current Electrodeposition

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Manganese dioxide samples were prepared by pulse current electrodeposition. The effects of the pulse current parameters on the type of hysteresis loop of the adsorption isotherms, the surface area, and nano-structure morphology of the samples were investigated in details by using the Barrett–Joyner–Halenda (BJH) method and the Scanning Electron Microscopy (SEM) technique. Results indicate that the applied duty cycles play key roles in different characteristics of the samples. Samples obtained at duty cycles up to 30% show a decreasing trend of the surface area as well as increasing grain size and represent a type H4 hysteresis as duty cycles decrease. At duty cycle of 30%, the surface area has been increased, whereas at higher duty cycle of 70%, a decrease in surface area and the grain size of samples has been observed. Even though type H2 hysteresis prevailed at duty cycles higher than 70%, an overlapping of both type H4 and H2 hysteresis loops were obtained at duty cycles lower than 70%. These behaviors were explained and discussed on the basis of the formation and dissolution mechanism of the passive layers during on- and off-times.

1. INTRODUCTION

Various types of Manganese dioxides (MnO$_2$) have been employed as catalysts and especially as electroactive materials in electrochemical capacitors and batteries. This is due to their great abundance, low cost, favorable charge density, high electrochemical and chemical stability and low toxicity. Preparation conditions of MnO$_2$ materials have great influence on its physico-chemical properties including nano-structures, morphology as well as chemical composition and porosity which translate into important electrochemical activities [1-5].

Electrodeposition is known to be a useful method for the preparation of MnO_2 [4-5]. Pulse current deposition technology is a new approach for the preparation of various types of technological important metal oxides. In this technique, the specific parameters are pulse current density (I_p), on-time (t_{on}), off-time (t_{off}), pulse frequency (f) and duty cycle (Θ) (Fig. 1). In this work, different pulse parameters (t_{on} and t_{off}) has been systematically applied during electrodeposition of manganese dioxide using a $MnSO_4/H_2SO_4$ electrolyte solution. In accordance with our previous results, it is found that the physico-chemical properties of MnO_2 are strongly related to the applied parameters [4]. We have further discussed the influence of these parameters on the porosity (including type of hysteresis loop on isotherms, surface area, and pore volume and pore size) and nano-structure morphology of MnO_2 samples.
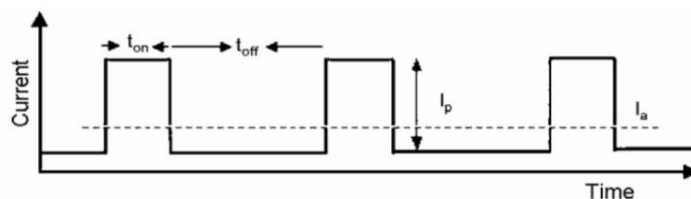

Figure 1. A schematic of the pulse current

2. EXPERIMENTAL

Electrodeposition experiments were carried out in an electrolyte solution containing $MnSO_4 \cdot H_2O$ (112 g/l) and H_2SO_4 (100 g/l) at a fixed temperature of 80 $^\circ$C.

Table 1. Pore characteristics of MnO_2 samples obtained at various pulse parameters.

samples	Frequency f	Duty cycle Θ	t_{on}	t_{off}	Pore diameter	Pore volume
	(Hz)	(%)	(mS)	(mS)	(nm)	(mL/g)
50Hz-2.5%	50	2.5	0.5	19.5	8.46	0.0232
50Hz-25%	50	25	5	15	3.98	0.0560
50Hz-92.5%	50	92.5	18.5	1.5	2.95	0.1114
250Hz-12.5%	250	12.5	0.5	3.5	2.99	0.0415
250Hz-25%	250	25	1	3	2.60	0.1127
250Hz-62.5%	250	62.5	2.5	1.5	3.09	0.0949
500Hz-10%	500	10	0.2	1.8	6.17	0.04304
500Hz-25%	500	25	0.5	1.5	5.03	0.0344
500Hz-50%	500	50	1	1	6.48	0.4474
500Hz-75%	500	75	1.5	0.5	5.68	0.2724
1000Hz-25%	1000	25	0.25	0.75	2.82	0.05826
1000Hz-50%	1000	50	0.5	0.5	6.27	0.0816
1000Hz-75%	1000	75	0.75	0.25	3.82	0.0899
10Hz-98.5%	10	98.5	98.5	1.5	4.78	0.140
DC	---	---	---	---	7.45	0.260

A Ti plate was used as the anode (area: 1 dm^2), which was centered between two Pb cathodes (area: 2 dm^2). The frequency has been changed from 10 to 1000 Hz, with variant duty cycles as shown in Table 1. Typical influential parameter of the pulse current electrodeposition including duty cycle, the peak pulse current (I_p) and off-time (t_{off}) on the nano-structure morphology of deposits (the grain size) have been considered in this study. Both t_{off} and I_p parameters, which can be changed simultaneously by changing duty cycles, are found to have opposite effects on the morphology of deposits. For example, the grain size showed an increasing trend with increasing t_{off}, whereas, the grain size decreased as the Ip increased [6]. Therefore, all electrodeposition were carried out at a constant peak current density (I_p) of 0.8 A/dm^2. As a consequence, the morphology could only be affected by the applied t_{off}. The Nitrogen adsorption isotherm was carried out by the Barrett–Joyner–Halenda (BJH) method (BELSORP-mini II, BEL Japan). Scanning electron microscopy (SEM), Philips model XL30, was used to study the morphology of the samples.
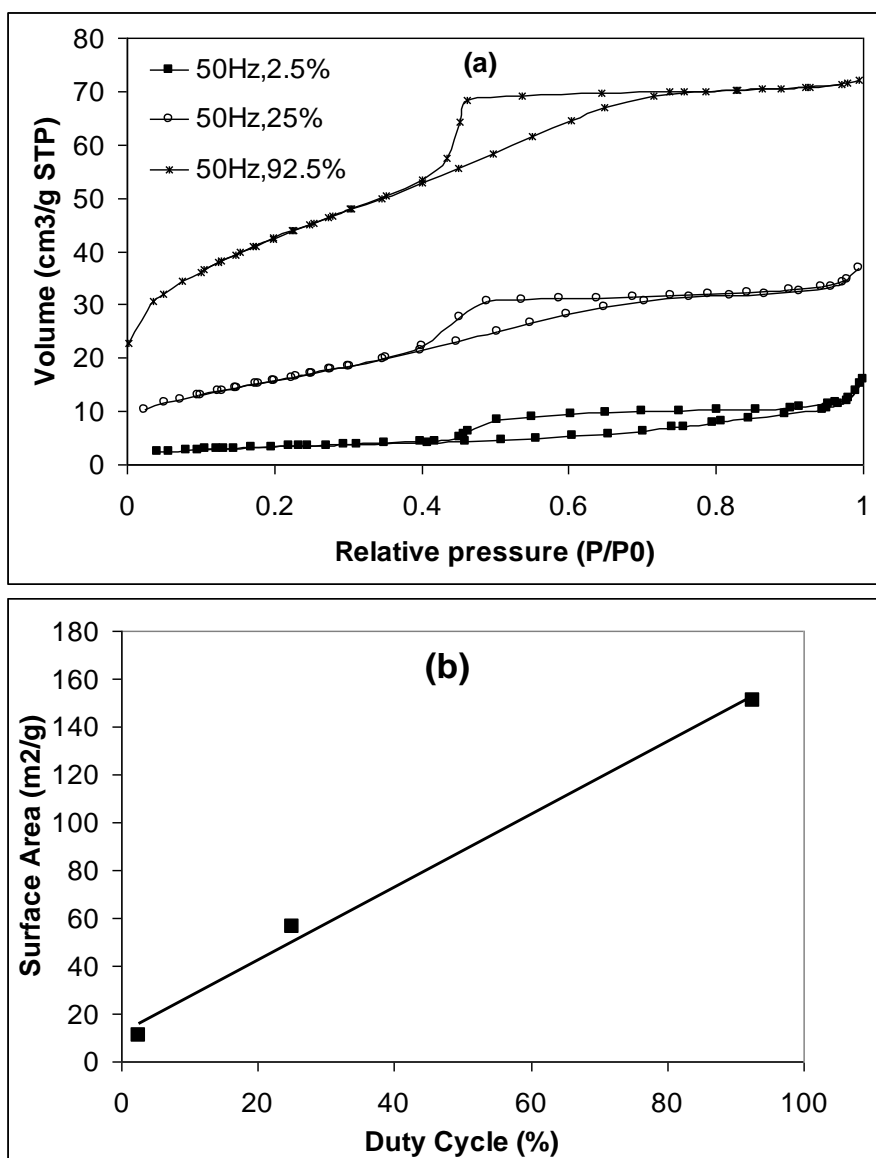

Figure 2. (a) Nitrogen adsorption isotherm and (b) the surface area of MnO$_2$ electrodeposited at 50Hz and variant duty cycles.

3. RESULTS AND DISCUSSION

Fig. 2-a shows the nitrogen adsorption isotherm of the MnO_2 samples, which are electrodeposited at f=50Hz and duty cycles of 2.5%, 25%, and 92.5%. The surface areas of samples are shown in Fig. 2-b. Fig. 3 illustrates the effect of duty cycle on the surface morphology of the samples.

In accordance to IUPAC classifications, all isotherms show a type IV pattern,. The hysteresis loop, which resulted from capillary condensation in the mesopores, is also seen in the samples. Preliminary information about the nature of the adsorbent was obtained by this classification. The shape and position hysteresis loop were affected by the morphology of the adsorbent (the specific pore structures and the degree of compaction) [7].

The 50Hz-2.5% isotherms remain nearly horizontal and parallel over a wide range of p/p_0. It is suggested this type of hysteresis can be ascribed to type H4, which it is often associated with narrow slit-like pores [8-9]. The surface area of 50Hz-2.5% sample is 11 m^2/g. The observed hysteresis loop for 50Hz-□25% has an intermediate shape between so-called types H2 and H4. Its surface area is 56 m^2/g. Many porous adsorbents (e.g., inorganic oxide gels and porous glasses) tend to give type H2 loops [7]. At higher duty cycle of 92.5%, completely type H2 could be observed as shown for the 50Hz-92.5% isotherm having a surface area of 151 m^2/g. A type H2 loop is believed to be associated with ink-bottle-like pores of varying radius, often generated by agglomerates or compacts of spherical particles of non-uniform size and arrangements.
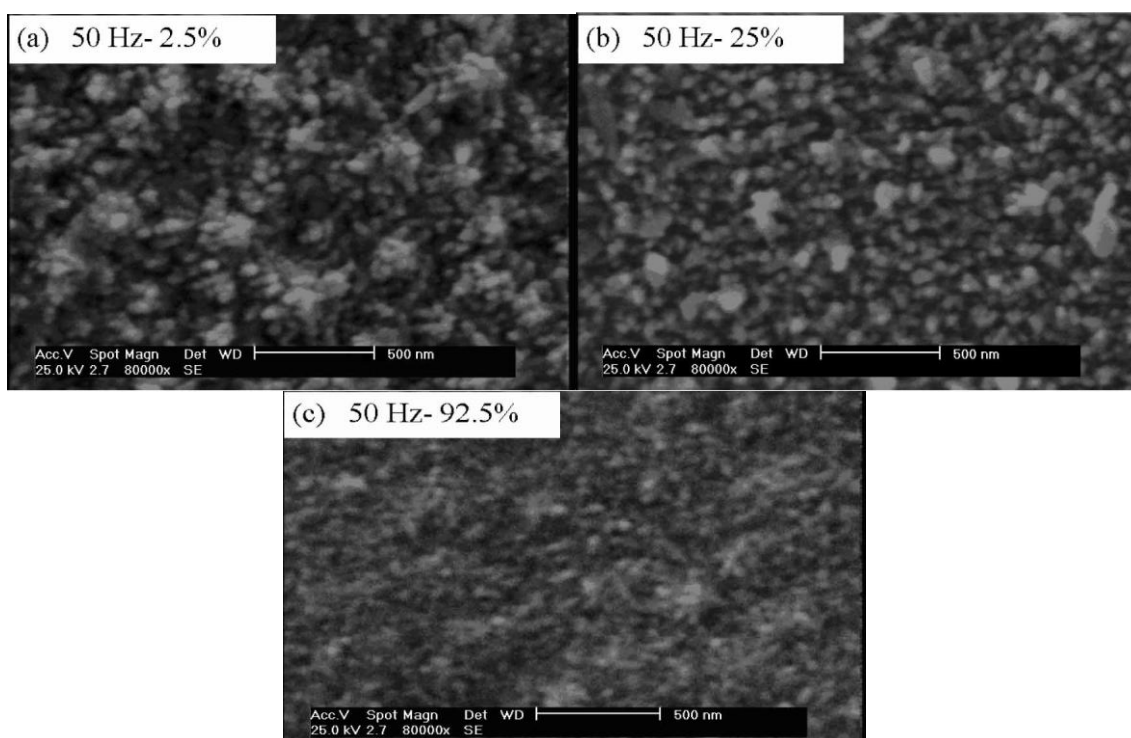

Figure 3. The SEM image of MnO_2 samples electrodeposited at 50Hz with various applied duty cycles.

A comparison between SEM images of the samples, which are prepared at 50Hz, allows us to conclude that the agglomeration of the particles is increased by increasing duty cycles (Fig. 3). As a consequence, we may expect a decreasing trend in the particle size of MnO_2 grains. The particle size of the samples prepared at 2.5%, 25% and 92.5% are about 65, 55 and 40 nm, respectively. Another point that should be considered is the increasing trend of the surface area of the samples with increasing duty cycles. As could be seen in Fig. 2-b, the highest surface area is obtained at a pulse frequency of 50Hz.
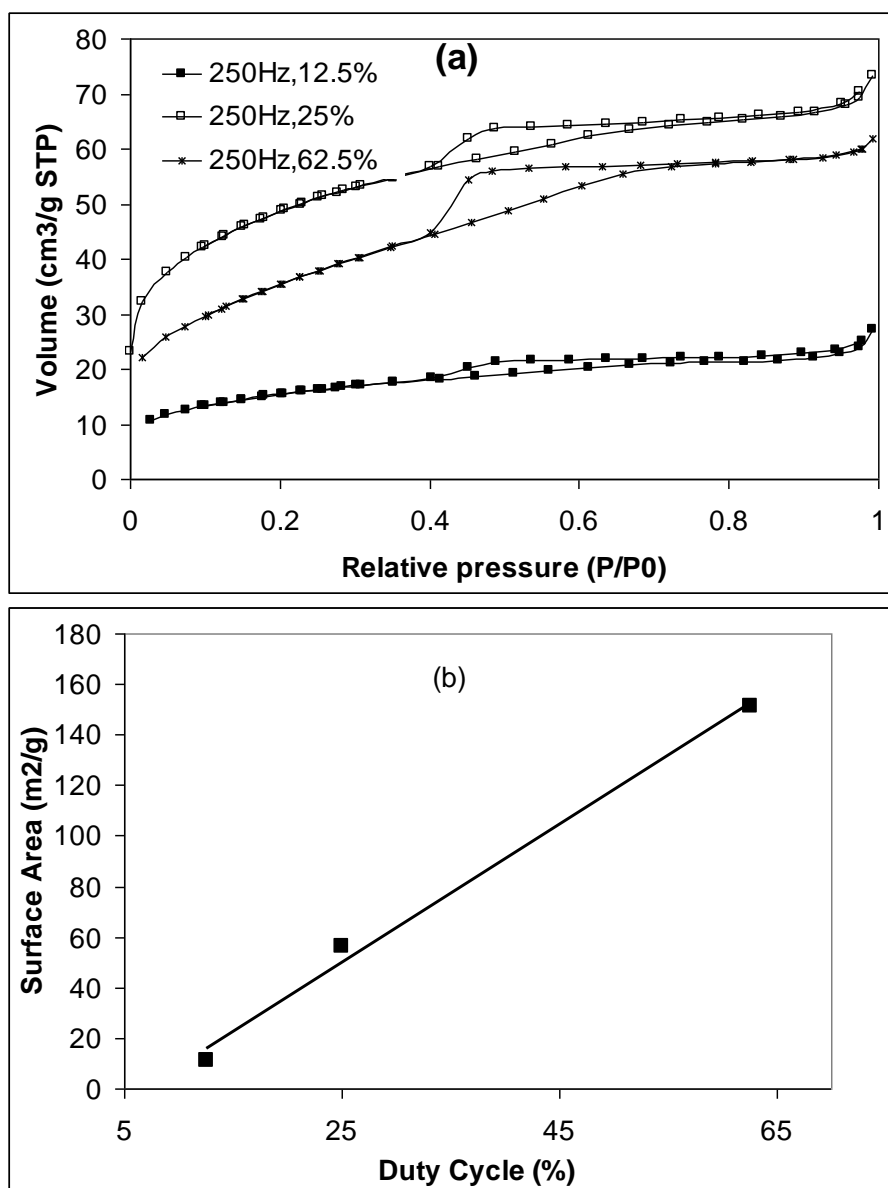

Figure 4. (a) Nitrogen adsorption isotherm and (b) the surface area of MnO_2 electrodeposited at 250Hz at various applied duty cycles.

The adsorption/desorption isotherm and the surface area of the samples, which are electrodeposited at 250Hz and at various duty cycles, are shown in Fig. 4. Similar to the previous cases, the sample electrodeposited at a low duty cycle of 12.5%, shows a type H4. By increasing duty

cycles from 25% and 62.5%, the contribution of type H2 is moderately increased. The isotherm obtained at 250Hz-25% belongs to a mix type of both H4 and H2, while that of 250Hz-62.5% belongs to type H2. Higher surface area could be obtained at higher duty cycles as evident in Fig. 4-b.
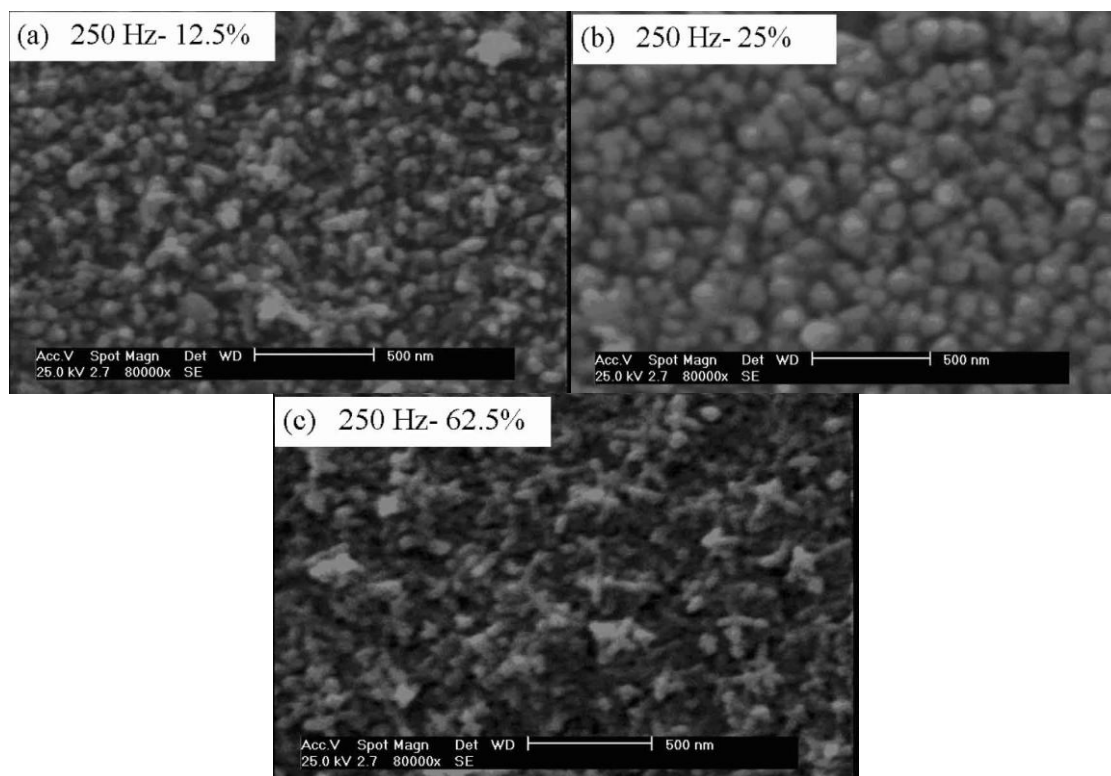

Figure 5. The SEM image of MnO_2 samples electrodeposited at 250Hz at various applied duty cycles.

Fig. 5 shows the SEM images of the samples obtained at 250Hz and at various duty cycles. The 250Hz-12.5% sample consists of almost aggregated particles with diameters in the order of 65 nm (Fig. 5-a). Fig. 5-b shows that, at a higher duty cycle, these particles closely link with each other and form larger particles as evidenced for the 250Hz-25% sample with relatively larger spherical particles of approximately 83 nm. The sample 250Hz-62.5%, which is deposited at a pulse frequency of 250Hz and at a duty cycle of 62.5%, exhibits particles having diameters in the range of 51 nm (Fig. 5-c). The large surface area of the latter could be explained on the basis of its algae-like structure (Fig. 4-b).

Fig. 6 shows the nitrogen adsorption isotherm and the surface area of the MnO_2 samples, which are electrodeposited at 500Hz and duty cycles of 10, 25, 50, and 75%. Fig. 7 illustrates the effect of the duty cycle on the surface morphology of the materials. It is clear that the application of lower duty cycles in the order of 10 and 25% again reveal the formation of type H4 with low surface area. Note that an increase in the duty cycle induces a change in surface morphology and significant changes in the surface area. As could be seen in Fig. 7-a, spherical particles of approximately 125 nm are formed in 500Hz-10% sample. The latter represents homogenous morphology and similar distribution in particles size and shape. An increase in duty cycle from 10% to 25% leads to a decrease in particle size (35 nm) and an increase in size of "interconnected nano-particles" (Fig. 7-b). Consequently, the

increase in the duty cycle induces the formation of finer deposits of nanoparticles with high compactness and uniformity.
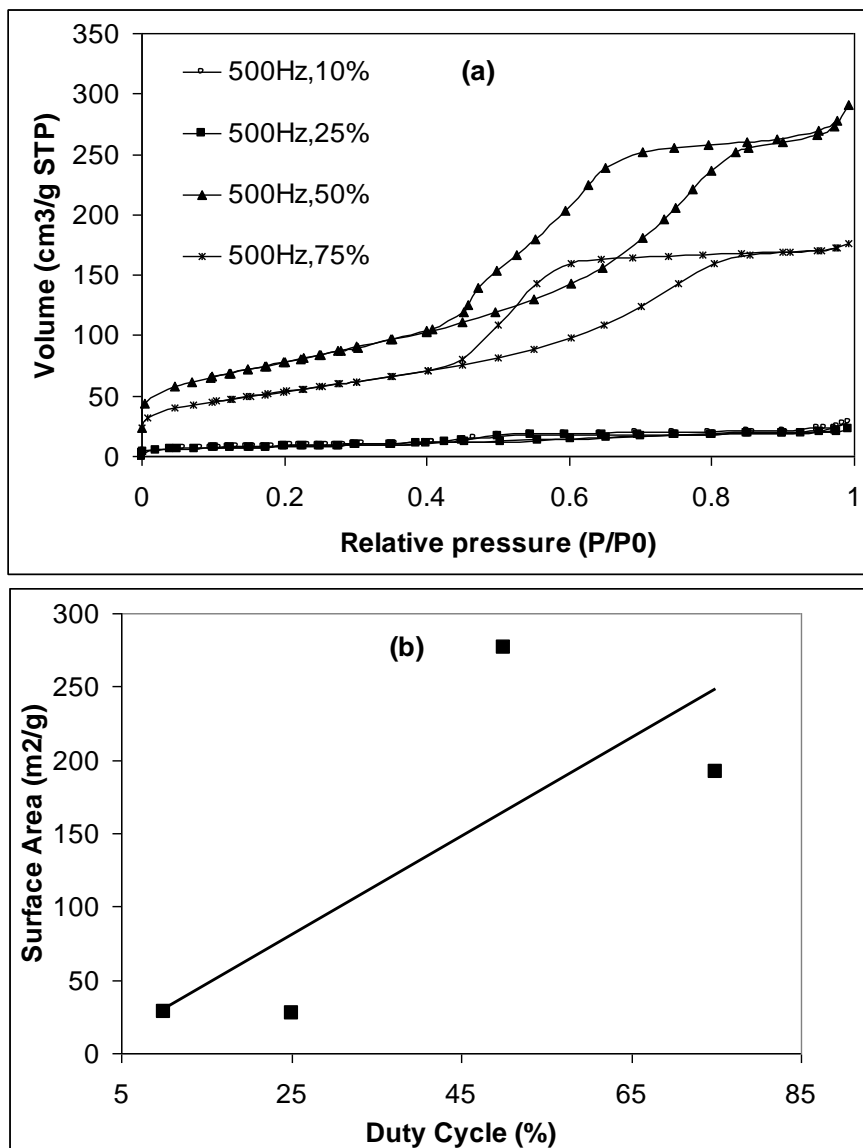

Figure 6. (a) Nitrogen adsorption isotherm and (b) the surface area of MnO_2 electrodeposited at 500Hz and various duty cycles.

We may expect that these phenomena could strongly affect the electrochemical performance of theses samples [4]. However, the effect of modifying parameters seems to be limited to changes in the surface area (~ 27 m^2/g) as could be observed for the special case namely the sample 500Hz-50%. The hysteresis loop, which is exhibited in the isotherm, is actually a mixture of types H2 and H3. A type H3 loop can be attributed to adsorbate condensation in capillary spaces between parallel plates or open slit-shaped capillaries. The SEM of this sample on the nanometer scale confirms this assumption. Fig. 7-c shows the possibility of obtaining oriented nano-sheets that are aligned or overlapped. The thickness of each nano-sheet was smaller than 30 nm. An increase in duty cycle from 25% to 50%

leads to a considerable increase in the surface area from 27 to 274 m^2/g (Fig. 6-b). The 500Hz-75% isotherm sample belongs to type H2. The 500Hz-75% sample clearly represents a nanostructure morphology in a three-dimensional network (Fig. 7-d).
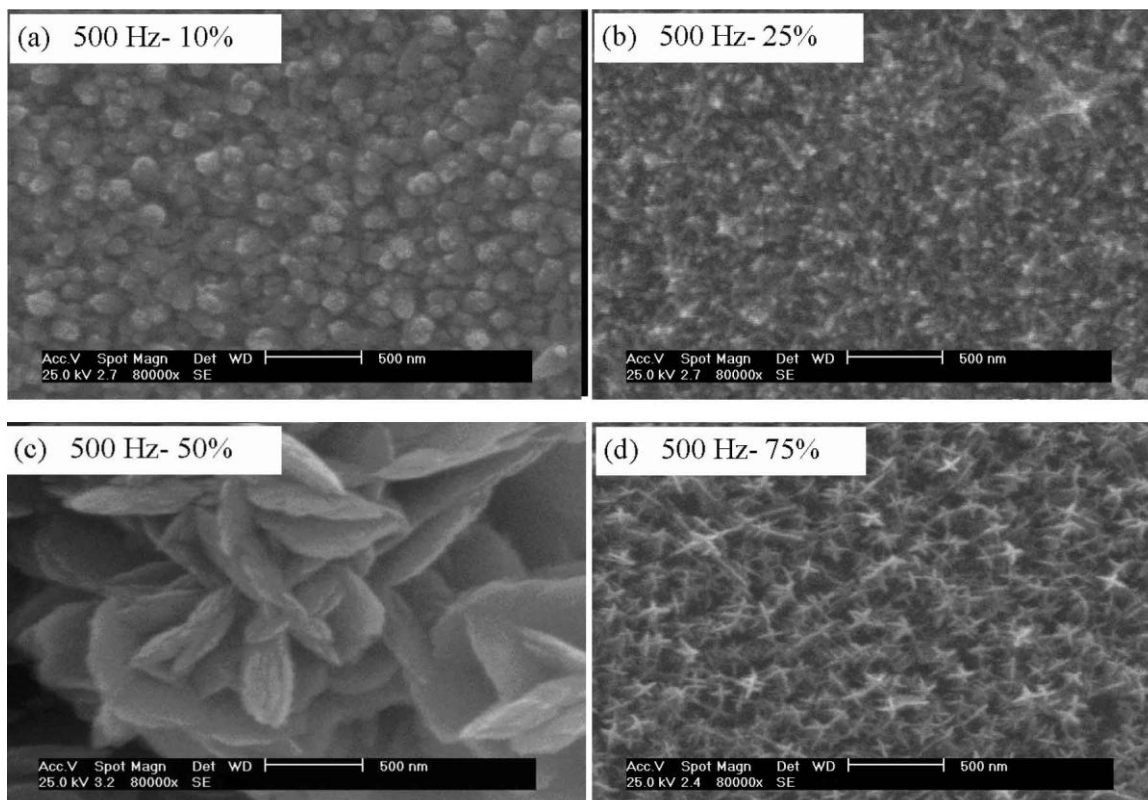

Figure 7. The SEM image of MnO_2 samples electrodeposited at 500 Hz and variant duty cycles.

Fig. 8 shows the adsorption/desorption isotherm, particle size and the surface area of the samples electrodeposited at 1000Hz. Fig. 9 shows SEM images different morphologies of three samples, which are electrodeposited at different duty cycles and at a fixed pulse frequency of 1000 Hz. The hysteresis loop observable in the isotherm determined on 1000Hz-25% is type H4 with a specific surface area of 83 m^2/g. It appears that this sample consists of micro- and meso- pores. Similar to other applied frequencies, the sample electrodeposited at low duty cycles ($\Theta<30\%$) consists of aggregate-like particles with diameters of 76 nm (Fig. 9-a).

The isotherm determined on 1000Hz-50% is overlapping types of all H2, H3 and H4. The isotherm determined on 1000Hz-75% is type H2. When an isotherm shows a very wide hysteresis loop, it is indicated that the obtained absorbent has a cage-like structure. In addition, the wide gap between the two curves implies an increased proportion of mesopores in the sample. The 1000Hz-50% is predominantly composed of mesopores while the 1000Hz-75% is composed of both micro- and meso- pores.

Application of the same t_{on} and t_{off} ($\Theta =50\%$) under 1000Hz frequency results in fine needle-like MnO_2 morphologies of 200–300 nm in length and 10–30 nm in diameter (Fig. 9-b).

Electrodeposition at 1000Hz-75% favors the formation of nano-spherical grains (Ø: 90 nm) of manganese dioxide.
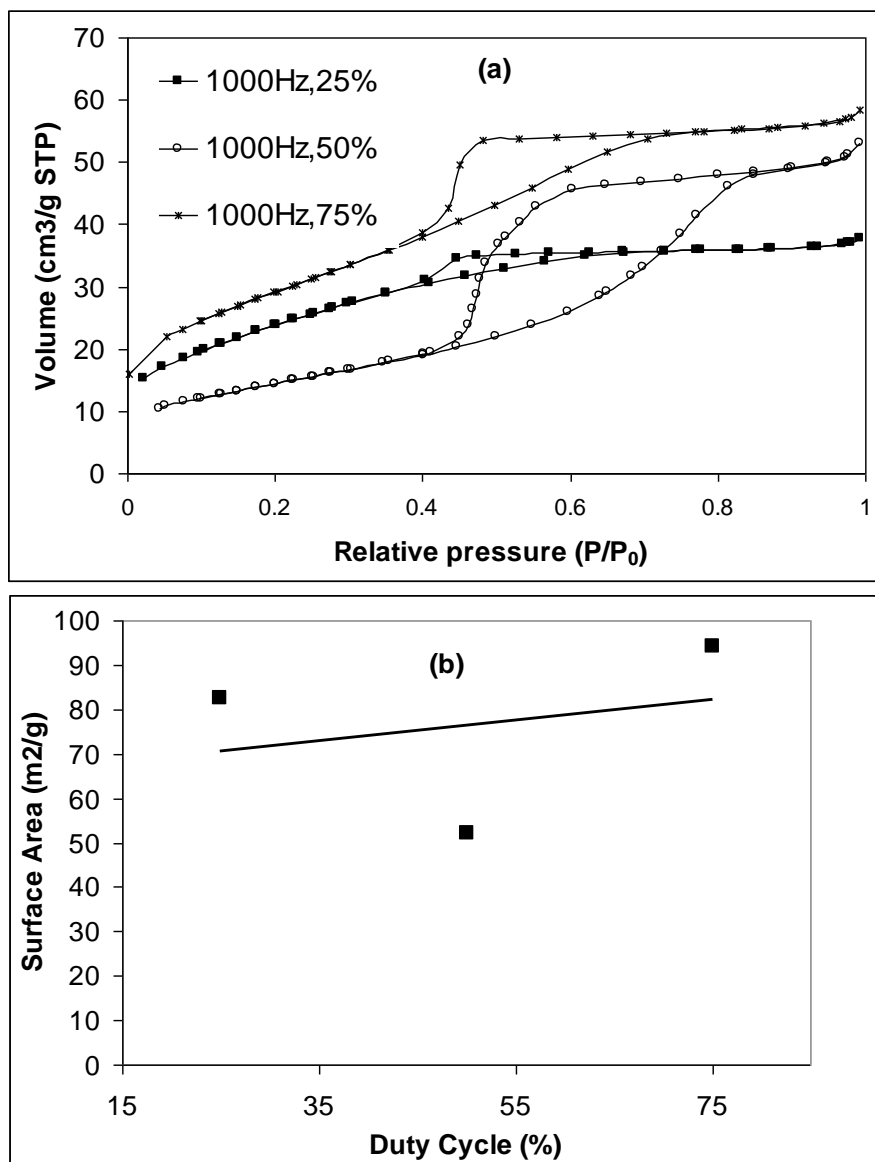

Figure 8. (a) Nitrogen adsorption isotherm pattern, and (b) the surface area of MnO_2 electrodeposited at 1000 Hz and variant duty cycles.

Fig. 10 gives the nitrogen adsorption isotherm and the surface area of the MnO_2 sample prepared at 10Hz-98.5% and direct current (DC) conditions. The isotherm of 10Hz-98.5% shows a sharp inflection of nitrogen adsorbed volume at P/P_0 of about 0.5 (type H2 hysteresis loop), which indicates the existence of mesopores. The surface area of 10Hz-98.5% is 118 m^2/g. Comparing the DC sample with pulse deposited samples, it is clear that DC strongly affected the porosity of MnO_2. The DC sample appears as an overlapping of types H2 and H3 with surface area of 140 m^2/g.

The electrodeposition of MnO_2 took place by successive oxidation of Mn^{2+} (reaction 1) and the accompanied disproportion reaction (reaction 2) [4-5, 10]:

$$Mn^{2+} \longrightarrow Mn^{3+} + e^- \qquad (1)$$

$$2Mn^{3+} + 2H_2O \longrightarrow MnO_2 + Mn^{2+} + 4H^+ \qquad (2)$$
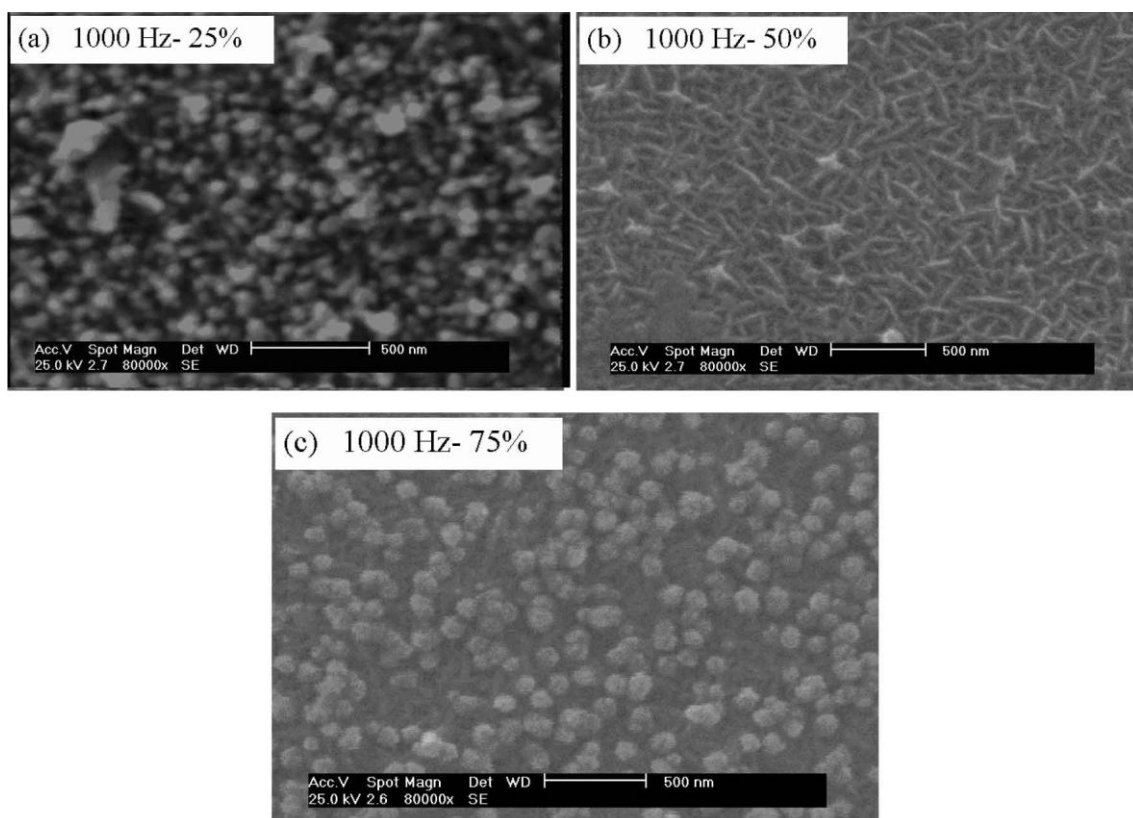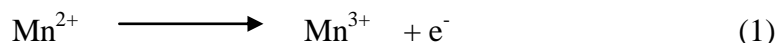

Figure 9. The SEM image of MnO_2 samples electrodeposited at 1000 Hz and variant duty cycles.

The formation of oxygen-containing intermediate Mn(III) species (e.g., MnOOH, $[Mn(H_2O)_6]^{3+}$, and Mn_2O_3) and, consequently, the growth of passive layers on the anode surface is inevitable during the electrodeposition of MnO_2. The physicochemical stability and thickness of passive layers play an important role in the morphology of the MnO_2 through the inhibition of the prevailing grains growth mechanism on the anode/electrolyte interface [5]. Furthermore, it is well known that the rate of formation, consumption, dissolving and/or the excess accumulation of oxygen-containing passive intermediate species are a function of the duration of both t_{on} and t_{off} [4]. The formation passive layers appear during t_{on} and these may be consumed in disproportion reaction (reaction 2) or accumulate at the anode surface. During t_{off}, dissolution and/or removal of the passive intermediate species could take place from the anode surface. Consequently, new and/or fresh sites are created after each off-time, which may be available as free sites for the next on-time. Thus, it may be

interpreted that the thickness of passive layers and consequently the magnitude of the active sites on the oxide surface are strongly affected by t_{on} and t_{off} and the t_{on}/t_{off} ratio.
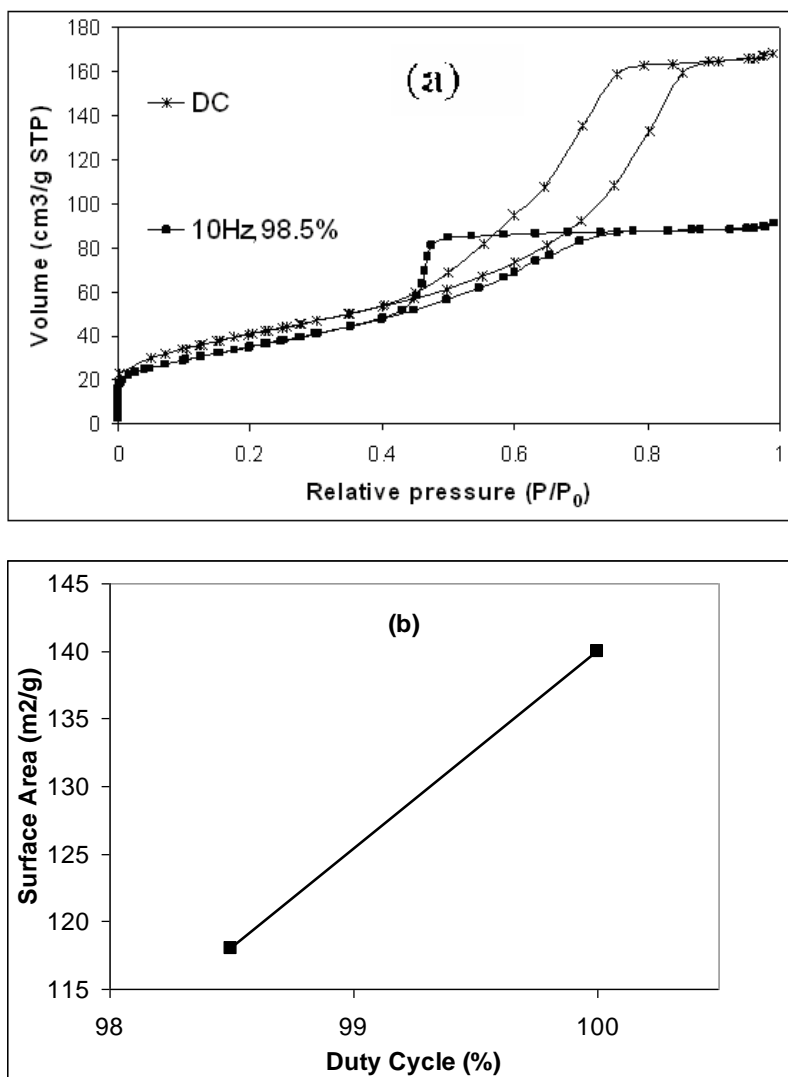

Figure 10. (a) Nitrogen adsorption isotherm and (b) the surface area of MnO_2 electrodeposited at 10Hz-98.5% and by direct current (DC).

The primary grains formed when the electrodeposition was started. If t_{on} is short and t_{off} is long (lower duty cycle), the amount of the formed passive oxygen containing intermediate species is low, because they would be either consumed in the next step or dissolved in electrolyte. Hence, there is no possibility for these species to accumulate at the surface of the grains. So, the surface of the grains acts like active/fresh sites and all outer surfaces of the grains contribute to electrodeposition at the next on-time. Consequently, these samples show large particle size without distinctive shapes. In addition, the lower duty cycle can cause the formation of denser products [4]. In accordance to these phenomena occurring on the anode surface, we may expect the formation of larger grains at lower duty cycles (e.g.

50Hz-2.5%, 500Hz-10%, 1000Hz-50%). As a second consequence, we may assume that only the spaces which are between grains can contribute to the adsorption/desorption process. As seen in the previous section, these samples generally belonging to type H4, which is often associated with narrow slit-like pores. Consequently, these samples generally have a low surface area with a wide pore diameter (Table 1).

The increase in the amount of the passive oxygen containing intermediate species could be attributed to application of higher duty cycles (t_{on} is longer and t_{off} is shorter; $50\% < \Theta < 90\%$). The on-time is long enough for the formation of passive intermediates and the off-time is short so there is not sufficient time for dissolving them leading to accumulation of these species at the deposit surface. At a higher t_{on}/t_{off} ratio, the passive layers block up the active centers to a larger extent and, consequently, the formation of new nuclei is prevailing in the process. As a result, these samples show finer particle size with a distinctive shape. As seen in the previous section, it is confirmed that formation of smaller grain is favored at higher duty cycles (e.g. 250Hz-62.5%, 500Hz-75%, 1000Hz-75%) and these samples generally belong to type H2. This type is often associated with pore cavities larger in diameter than the openings (throats) leading into them (often referred to as *ink bottle pores*). The ink bottle pores may be formed by the presence of a passive intermediate at the orifice of a pore. In this case, the grain growth is prevented because of the higher stability of the Mn (III) species and the increasing thickness of the passive layers. These conditions lead to the production of the ink bottle pores with cavities that are larger in diameter than the openings (throats). Consequently, by increasing the duty cycle, the amount of type H2 increased and the amount of type H4 decreased. As on can see, the 500Hz-10% and 500Hz-25% samples are type H4, 500Hz-50% sample is a mixture of both types H4 and H2, and lastly, 500Hz-75% is type H2. The surface area increased by increasing the duty cycle. Similar results are seen at other frequencies and at 10Hz-98.5%. Generally, with the approach of pulse current to direct current (increasing duty cycle), the accumulation of the barrier passive layer can be increased. As a consequence the physico-chemical properties (especially the porosity) of MnO_2 could be strongly influenced by the applied pulse parameters.

4. CONCLUSION

The influence of the pulse deposition parameters on the porosity of MnO_2 electrodeposited from an aqueous solution was investigated. The hysteresis are visible in the nitrogen adsorption isotherm patterns of all samples. The samples obtained at the low duty cycles ($\Theta < 30\%$) show similar characteristics as to the type H4 adsorbents. With the increasing duty cycle, type H2 structures grow moderately resulting in a mixture of types H4 and H2 at $30\% < \Theta < 70\%$. Formation of type H2 is favored at duty cycles higher than 70% ($\Theta > 70\%$). The surface area of the resultant MnO_2 generally increases with increasing duty cycles. The dramatic change in the isotherm characteristics (hysteresis loop shape) and the surface area is a consequence of the applied duty cycles and pulse frequencies. This proves that fundamental changes in physico-chemical properties and specially changes in nano-structures occur in the samples. We may conclude from the experimental results that the morphology of samples is affected by the formation of passive layers due to the presence of oxygen containing

intermediate Mn(III) species. By adjusting the applied pulse parameters, nano-tailoring of manganese dioxide in different morphological varieties is possible.

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