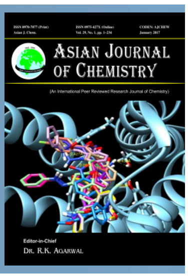
Asian Journal of Chemistry; Vol. 29, No. 9 (2017), 2016-2024

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20743



Cyclic Voltammetry and Electrochemical Impedance Spectral Properties of MnO_2 Obtained by Waste Discarded Batteries Using Eco-Friendly Leaching Materials

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Received: 1 May 2017; *Accepted*: 21 June 2017; *Published online*: 15 July 2017; AJC-18486

This paper reports the recovery of zinc and manganese using hydrometallurgical method from spent dry cell batteries. For the recovery of zinc and manganese present within the spent dry cells are meted out by two acidic subtractive leachants specifically oxalic acid and hydrogen peroxide. The chemical analysis of metals from dry cell batteries were performed by using atomic absorption spectroscopy (AAS). The fundamental composition of recovered metals from dry cell batteries were confirmed by energy dispersive X-ray analysis (EDAX). The section composition of the recovered metals from dry cell batteries were confirmed from X-ray diffractometer. Surface morphology of the recovered metals were examined using scanning electron microscopy (SEM). The functional group analysis were done by Fourier transform infrared (FTIR) analysis. Oxalic acid and hydrogen peroxide were showing active leachants on the recovery of zinc and manganese. Leaching yields of both zinc and manganese higher at leach temperature of 90 °C and NaOH was used as precipitating agent for the recovery of Mn as MnO_2. The cyclic voltammetry (CV) shows the more reversibility of the electrode and electrochemical impedance spectroscopy (EIS) reveal charge transfer resistance (R_{ct}) and capacitance of electrode. The electrode using 0.5 M NaOH has lowest R_{ct} and more capacitance among all the electrolytes, indicating better conductivity and confirmed that the charge transfer resistance and capacitive behaviour is faster.

Keywords: Waste dry cell, Leachants, Electrochemical, MnO_2, Zinc, Manganese, Cyclic voltammetry.

INTRODUCTION

Spent alkaline batteries signifies a severe pollutant in terms of heavy metals content when discarded improperly [1,2]. Zinc and manganese cell batteries represents a major amount of spent batteries wastes. The discarded spent alkaline batteries shows severe environmental problem because they contains comparatively high concentration of hazardous metals in their electrodes. The consequences are a greater need of landfills for disposal of the wastes and a more intensive exploitation of mineral resources. Moreover, the local authorities are unable to give the authorization for the opening up of new landfills due to the costs to maintain landfills. During the last decades, to match the environmental requirements the battery producers were involved in the research to find out the substitute for toxic substances still used in the batteries.

Different types of batteries, such as Zn-air battery, zinc-manganese dioxide battery (Zn-MnO_2) and zinc-carbon (Zn-C) are a source of valuable metals like Zn and Mn. Their recovery represents an economic benefit for the battery producers and bring to smaller volume to dispose, thus it lengthening the life of landfills [3]. The recovered metals from spent alkaline batteries are used for different electronic applications such as remote communications, torches, military radio receivers, electronic gadgets, some medical devices and electronic toys, *etc*. These batteries are composed of a cathode, anode, electrolyte and a separator [4,5].

From literature review, numerous reduction approaches in acid media has been investigated such as lactose reduction leaching [6], sucrose reduction leaching [7], corncob reduction leaching [8], oxalic acid reduction leaching [2], hydrogen peroxide reduction leaching [9], ascorbic/oxalic acid reduction leaching [10,11] and activated carbon powder reduction leaching [12]. Many patented processes have already been developed mainly for treatment of dry cell batteries for a mixture of batteries [13], for lead-acid [14] and a hydrometallurgical process for the recycling of all cell components using sulfuric acid leaching with waste carbohydrates as reducing compounds [15]. Acidic leaching is a possible process with recovery of almost 100 % of zinc as soluble form $ZnSO_4$ [16,17]. A similar result was obtained using 0.7 % (v/v) H_2SO_4 at 70 °C and time 3 h [18]. Many studies have focused on reductive leaching of tetravalent manganese using organic reductants, including sucrose, glycerine [7,19] and triethanolamine and thiosulfate [20,21]. At similar conditions [22], found Mn as 40 % and similar medium for recovery of zinc and manganese from alkaline and zinc-carbon spent batteries [17].

Most of the researchers needed for various variabilities of strategies for employing of those primary batteries, were primarily in Japan, China, Korea, Europe and India [23]. The pyro metallurgic processes are comparatively straightforward, however, they aren't applicable owing to the high energy needs and also the emission of harmful gases within the environment. The hydrometallurgical strategies are the foremost common methods altogether over the globe as a result of its environmentally appropriate and economical to treat even low metallic element containing materials on a small scale with high purity and low energy needs. Hence, the treatment of those wastes for the recovery of Zn and Mn is vigorous for discarded material to material utilization. Thus, the assembly of consumed alkaline batteries and its unwanted waste is enlarged dramatically day by day within the environment. Zinc metal oxidized to ZnO and MnO_2 reduced to Mn_2O_3 once being discharged and these products were used for present study [24,25]. The main objective of this study was to search the recovery and leaching of Zn and Mn from discarded alkaline batteries and cyclic voltammetry and electrochemical impedance spectroscopy studies of MnO_2 obtained from leach solutions. In this study, a hydrometallurgical leaching by oxalic acid and hydrogen peroxide were reductant in sulfuric acid media. At constant temperature (90 °C), the three aspects verified were battery powder, acid concentration and oxalic acid concentration.

EXPERIMENTAL

The experimental studies made use of a mixture of various sizes of spent primary batteries were collected from different manufactures. Concentrated H_2SO_4, $H_2C_2O_4{\cdot}2H_2O$ and H_2O_2 of analytical grade were used and that they were provided by Merck.

Battery dismantling and leaching procedure: Spent primary batteries were collected from many manufacturers and so manually dismantled and just about 500 g of powder was extracted. Then the powder was grounded and washed with water. Washed powder was dried for 24 h at 100 °C. Sample showed a weight loss of 5.7 % when drying, therefore the powder wetness was simply determined. Leaching tests were performed in a 250 mL closed (iodine) flask. Solution was heated at 90 °C by a controlled temperature heater equipped with magnetic stirrer (250 rpm) (REMI 1 MLH). For each test, the solution mixture was made freshly ready by dissolving the desired quantity of analytical grade oxalic acid and washed battery powder in 100 mL of H_2SO_4 solution, consistent with the experimental arrange. During each test, 1 mL of leach liquor was withdrawn after 1, 3 and 5 h severally to measure the concentration of Zn and Mn by atomic absorption spectroscopy exploitation GBC Avanta Ver 1.33 Analysis 1.

Each sample was diluted 1:10 by acidic solution of HNO_3 (pH ~ 2) to avoid precipitation of metals and keep at 5 °C. Once in 5 h, when reactions were stopped, hydrogen ion concentration (pH) was measured and also the mixtures were filtered, washed and placed in the oven at 100 °C. After 24 h, solid residues were recovered and weighed to measure the weight loss. This quantitative analysis was repeated at room temperature using a completely different reductants (1 M H_2O_2) in a 100 mL of 3 M H_2SO_4 resolution with a solid to liquid ratio 1:10 and 250 rpm magnetic stirring. The possible products of the leaching of spent dry cell with reducing agents were shown in Fig. 1.

Leaching tests with sulphuric acid-oxalic acid: In the present work, a factorial design was chosen for conducting the leaching tests when the investigated variables were battery powder, oxalic acid, sulphuric acid concentration and temperature. The degree of variables are given in Table-1.

TABLE-1
FOR Zn AND Mn LEACHING BY
OXALIC ACID IN H_2SO_4 SOLUTION

S. No	Factor	Low level	High level
I	Powder concentration (%)	10	20
II	Oxalic acid concentration (g/100 mL)	2.97	5.94
III	Sulphuric acid concentration (M)	0.9	3.0
IV	Temperature (°C)	90	90

Leaching tests with sulphuric acid-hydrogen peroxide: The natural action tests with the second acidic-reductive leaching system were performed on the idea of a factorial design analogue to it of the primary leaching system except for factor IV, which was fixed at room temperature. In these tests, temperature wasn't investigated at larger values for the stability problem of the hydrogen peroxide. The levels of variables are given in Table-2.

TABLE-2
FOR Zn AND Mn LEACHING BY HYDROGEN
PEROXIDE IN H_2SO_4 SOLUTION

S. No	Factor	Low level	High level
I	Powder concentration (%)	10	20
II	H_2O_2 concentration (M/100 mL)	0.032	1
III	H_2SO concentration (M/100 mL)	0.9	3
IV	Temperature (°C)	27	27

Recovery of MnO_2 from dry cells: Recovery of manganese as MnO_2 from the leaching solution is feasible at room temperature while not special purification of the solution and maintaining a high potency. After the complete reductive acid leaching process, selective precipitation test was carried out at room temperature. Required quantity of leached solution in a 500 mL beaker was taken and a solution of 4 M NaOH was added slowly to the beaker covering leach solution with constant stirring by magnetic stirrer. At the end of precipitation, the solution in the beaker was filtered and the solid residue that remained in the filter paper was dried in an oven at 100 °C for 2 h. MnO_2 was obtained from dry cell batteries leaching solutions and the following reactions had taken place are shown in eqns. 1 and 2:

$$MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4 \qquad (1)$$

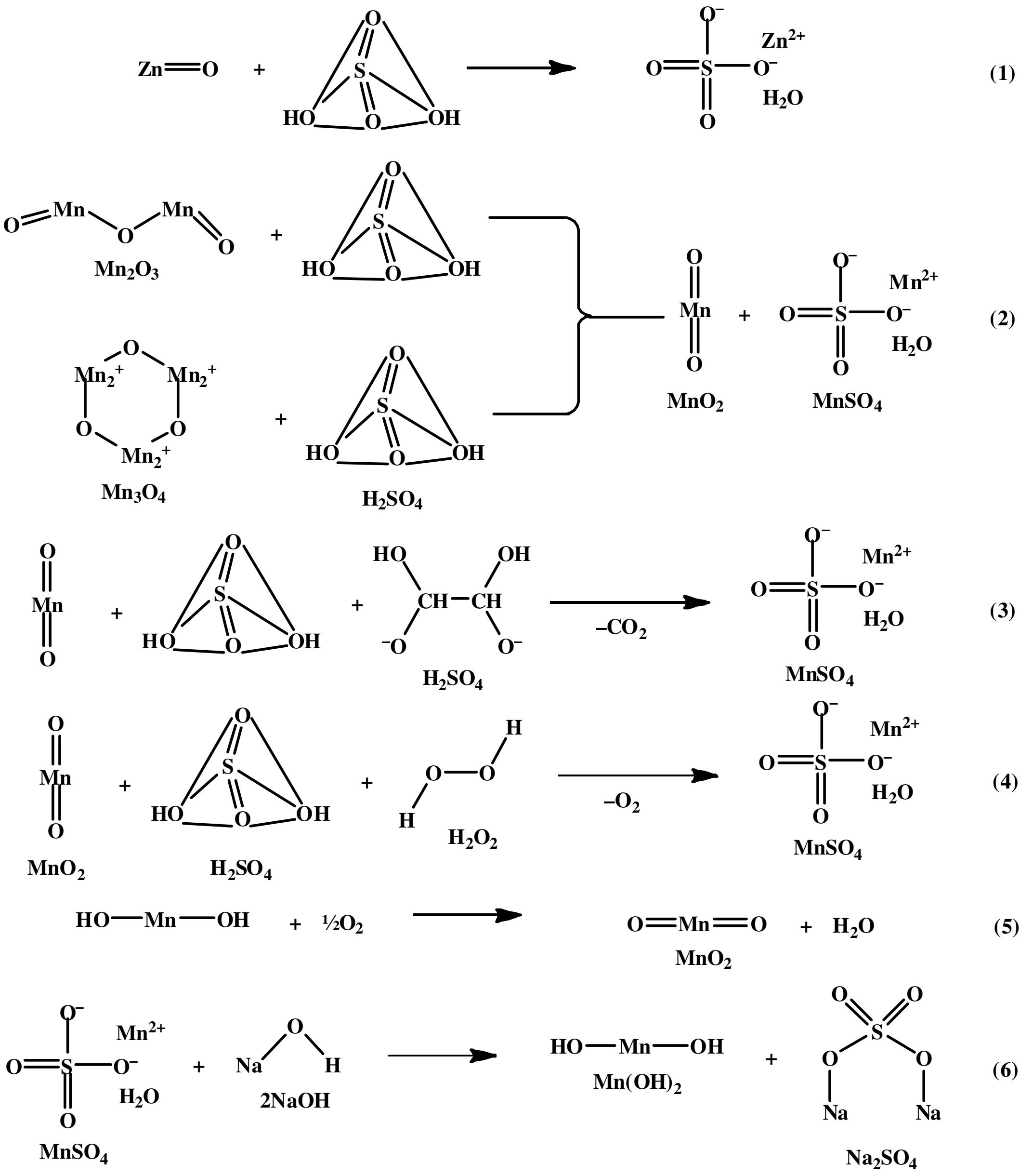

Fig. 1. Possible products of the leaching of spent dry cell with reducing agents

$$Mn(OH)_2 + 0.5O_2 \longrightarrow MnO_2 + H_2O \quad (2)$$

Characterizations: X-ray diffraction studies were carried out using a high resolution X-ray diffractometer Maxima-7000 (Shimadzu) at a scanning rate of 2° min^{-1} using CuK_α radiation (λ = 1.54 Å) operating at 40 kV and 30 mA. The distribution of Zn and Mn within the battery was studied using SEM (SU-1500, HITACHI). The accelerating potential was 15 kV and the beam current was 20 mA. The FTIR spectrum was recorded on Perkin Elmer FTIR 1650 spectrophotometer at ambient temperature using a KBr disk method. The disk containing 0.0010 g of the sample and 0.3000 g of fine grade KBr was scanned with 16 scans at wave number range of 4000-400 cm^1. Atomic absorption spectroscopy (AAS) for the quantitative determination of chemical elements of Zn and Mn from leached solution using GBC Avanta AAS version 1.33. Electrochemical measurements such as CV and electrochemical impedance were carried out using CH electrochemical work station.

RESULTS AND DISCUSSION

Leaching tests with H_2SO_4-oxalic acid and H_2SO_4-H_2O_2: To know the impact of sulphuric acid concentration on zinc and Mn dissolution, the leaching tests are carried out for each at 0.05 to 3 M concentration, a solid liquid ratio 1:10 (g/mL), stirring speed 250 rpm and leaching temperature 90 °C for 5 h. From the tests, it was observed that the 99.25 % of zinc, 86.03 % of manganese in oxalic acid (Table-3) and 98.8 % of Zn and 81.56 % Mn were present in hydrogen peroxide (Table-4), respectively. The dissolution was enhanced considerably with increasing sulphuric acid concentration up to 1.8 M and further enhanced up to 3 M concentration and it remained constant as shown in Fig. 2a and 2b. These results revealed that H_2SO_4 concentration was highly effective on dissolution of zinc and manganese from dry cell powder. To dissolve zinc and manganese, oxalic acid and hydrogen peroxide were used as reducing agents to improve zinc and manganese dissolution.

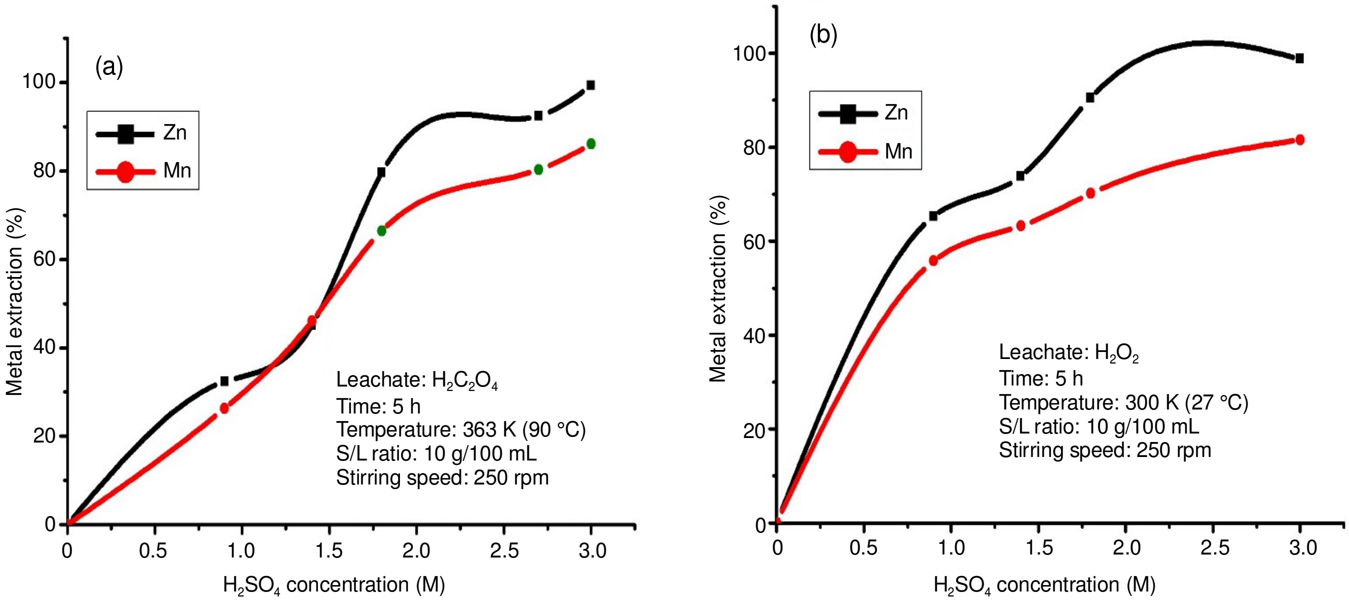

Fig. 2. Effect of H_2SO_4 concentration on Zn and Mn using (a) $H_2C_2O_4$ and (b) H_2O_2 leachants

TABLE-3
RESULTS OF THE FACTORIAL DESIGN AFTER 5 h LEACHING BY OXALIC ACID

Sample	I (g)	II (g)	III (M)	IV (°C)	Concentration (g/dm^3)		pH	Weight loss (%)
					Zn	Mn		
1	10	8.90	0.9	90	32.40	26.30	1.789	32.40
2	10	2.97	1.4	90	45.03	46.07	0.457	37.71
3	20	5.90	1.8	90	79.60	66.38	0.355	42.65
4	20	5.94	2.7	90	92.36	80.27	0.152	50.15
5	10	2.97	3.0	90	99.25	86.03	0.040	53.90

TABLE-4
RESULTS OF THE FACTORIAL DESIGN AFTER 5 h LEACHING BY HYDROGEN PEROXIDE

Sample	I (g)	II (g)	III (M)	IV (°C)	Concentration (g/dm^3)		pH	Weight loss (%)
					Zn	Mn		
1	10	0.096	0.9	27	65.30	55.80	0.566	50.24
2	20	0.192	1.4	27	73.85	63.23	0.270	62.54
3	20	0.064	1.8	27	90.05	70.13	0.320	60.29
4	10	1.000	3.0	27	98.80	81.56	0.030	54.50

Energy dispersive X-ray spectrometer: Energy dispersive X-ray analysis (EDX) was used to obtain the elemental composition of the metals in dry, washed and leach powder were shown in Figs. 3 & 4 and Table-5. In Fig. 3a, indicating the presence of Zn and Mn are the elements in the dry powder with presence of Cl, Fe, S and Al. The existence of Cl is attributable due to NH_4Cl that was used as electrolytic material in dry cell batteries. In Fig. 3b shows that a presence of sulphur in the washed powder that was originated from elemental sulphur. After leaching with oxalic acid and hydrogen peroxide were used as reductants, clearly shows expressive quantity of Mn and Zn within the sample as shown in Fig. 4a and Fig. 4b. However, the leached powder using reductants, illustrated that the large quantity of Mn content in the sample and marginal quantity of Zn were obtained. This is often attributable to reductants reduces and soluble from MnO_2 to Mn^{2+} sulphuric acid solution but not for the Zn. Hence in washed powder the quantity of Mn is increased.

TABLE-5
EDAX ANALYSIS OF SPENT ALKALINE
BATTERIES AND RECOVERED MnO_2

Sample	C (%)	Zn (%)	Mn (%)	O (%)	Fe (%)	S (%)
Dry powder	64.5	17.0	6.66	4.87	1.78	0.50
Washed powder	62.6	8.68	6.20	11.2	0.31	10.9
Leach with oxalic acid	42.3	24.3	25.3	6.20	1.32	-
Leaching with H_2O_2	49.3	2.6	36.8	9.40	1.9	-
Recovered MnO_2	-	-	93.17	6.87	-	-

X-ray diffraction study: X-ray diffraction of dry, washed powder and leaching with oxalic acid and H_2O_2 were shown in the Fig. 5a to 5d and the zinc oxide and manganese oxides (Mn_2O_3, Mn_3O_4 and MnO_2) were the main components in all the spectra. In Fig. 5a indicating the presence of potassium superoxide is accredited to the reaction of KOH with oxygen that may take place during the dismantling process as shown in the eqn. 3. In Fig. 5b, iron oxide (Fe_2O_3) content was detected in the spectrum formed in the dismantling process, which initiated contamination of the sample or from corroded or oxidized batteries.

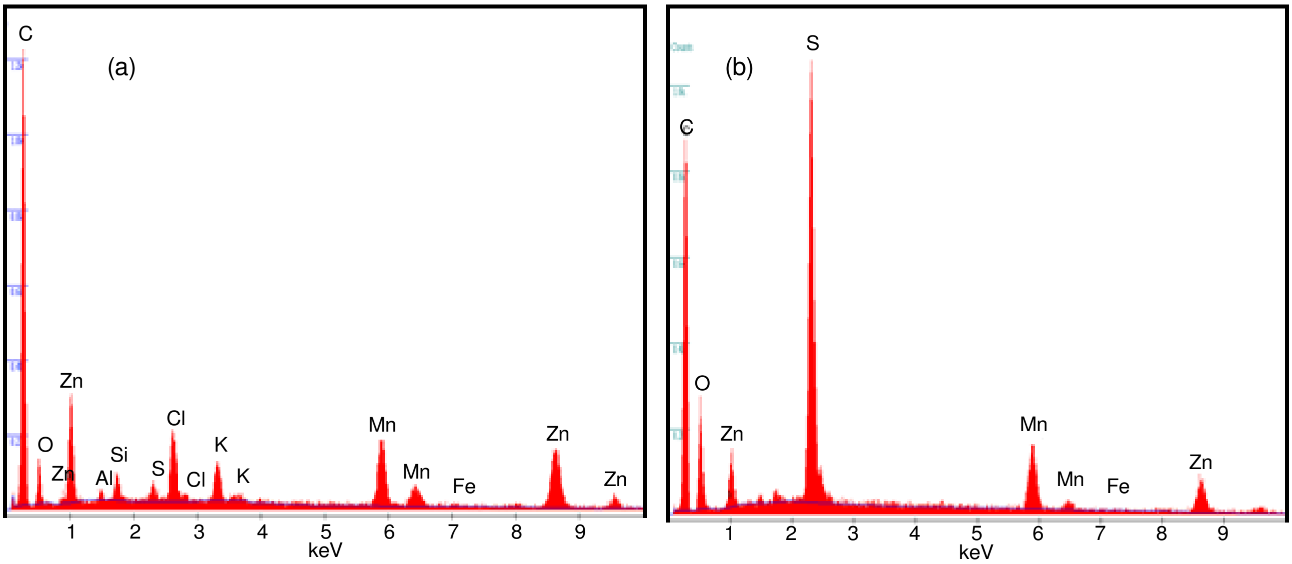

Fig. 3. EDAX images of spent batteries (a) dry powder (b) washed powder

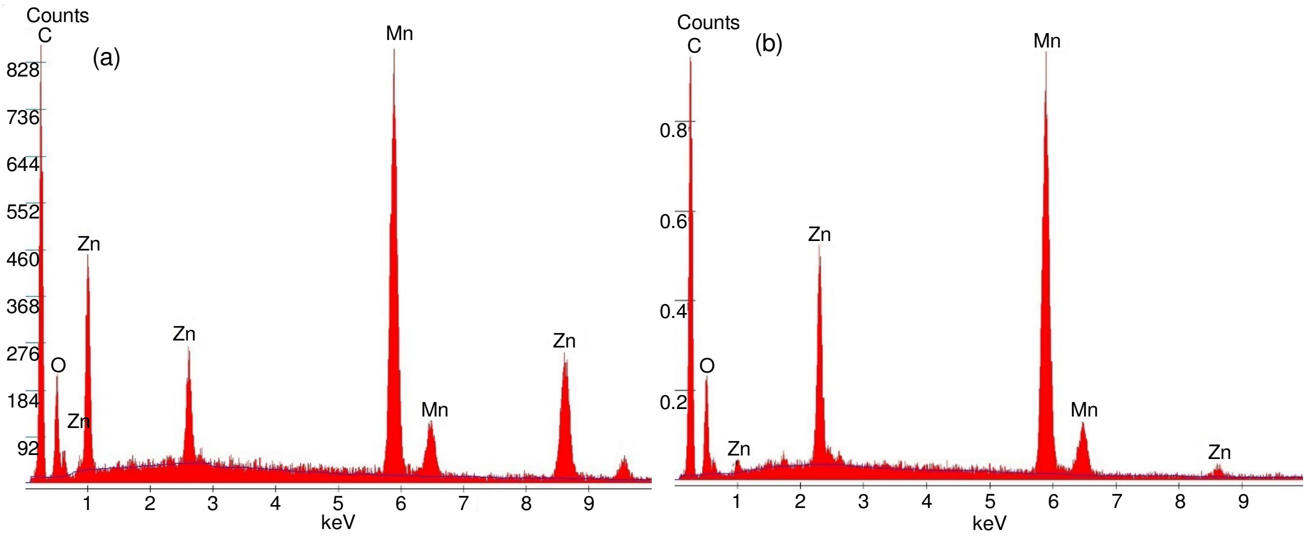

Fig. 4. EDAX images of spent dry cell batteries leaching with (a) $H_2C_2O_4$ (b) H_2O_2

$$KOH + O_2 \longrightarrow KO_2 + H_2O \qquad (3)$$

According to literature review, chloride and potassium are due to the electrolyte of dry cell batteries [18]. After washing, it is clearly well-known that K and Cl reduced by about 83 and 93 %, respectively because of their solubility. The leaching with oxalic acid as shown in Fig. 5c indicating the zinc oxide and manganese oxide phases with more intense 2θ value and in Fig. 5d leaching with hydrogen peroxide showing the less Zn and Mn components in the spectra.

Scanning electron microscopy: Scanning microscopy (SEM) was used to study the morphology of the dry, washed powder and its leach residues as shown in Fig. 6a to 6d. In Fig. 6a the dry powder shows the particles are agglomerated and in Fig. 6b clearly indicating the impurities are removed after washed with water and H_2SO_4 and the zinc and manganese particles are almost agglomerated in the powder. In Fig. 6c, shows that zinc particles are having hexagonal shape and zinc and manganese particles are well distributed throught and little agglomeration and in Fig. 6d indicating the particle are uniform distribution and the particle size range from 50 μm.

Fourier transfer infrared spectrometer: FT-IR spectra of dry, washed powder and leaching residues were shown in Fig. 7a and 7b. The bands at around 3452, 3352 and 1627 cm^{-1} correspond to the O-H vibrating mode and 1119, 1114 and 1083 cm^{-1}, respectively and 1180 cm^{-1} corresponds to C-O stretching which can be ascribed due to accumulation of sulphuric acid in the dry and washed powder. The bands located at 636, 621 and 601 cm^{-1} belong to the metal-oxygen bending vibrations of Zn-O and Mn-O in powder as shown in Fig. 7a. In Fig. 7b the bands 3600, 3400, 2700 and 2400 cm^{-1} correspond to O-H stretching mode and 1500, 1400 and 900 cm^{-1} C-H vibrating mode of oxalic acid and hydrogen peroxide were leachants in the recovery of Zn and Mn.

EDAX analysis of manganese dioxide: The dried solid residue was characterized by the EDX-SEM to analyze elemental composition and morphology of the powder as shown in Fig. 8. The chemical composition of the manganese dioxide was qualitatively determined by EDAX micro-analysis as shown in Table-5. EDAX analysis only detects manganese and oxygen as components of the deposit. The composition

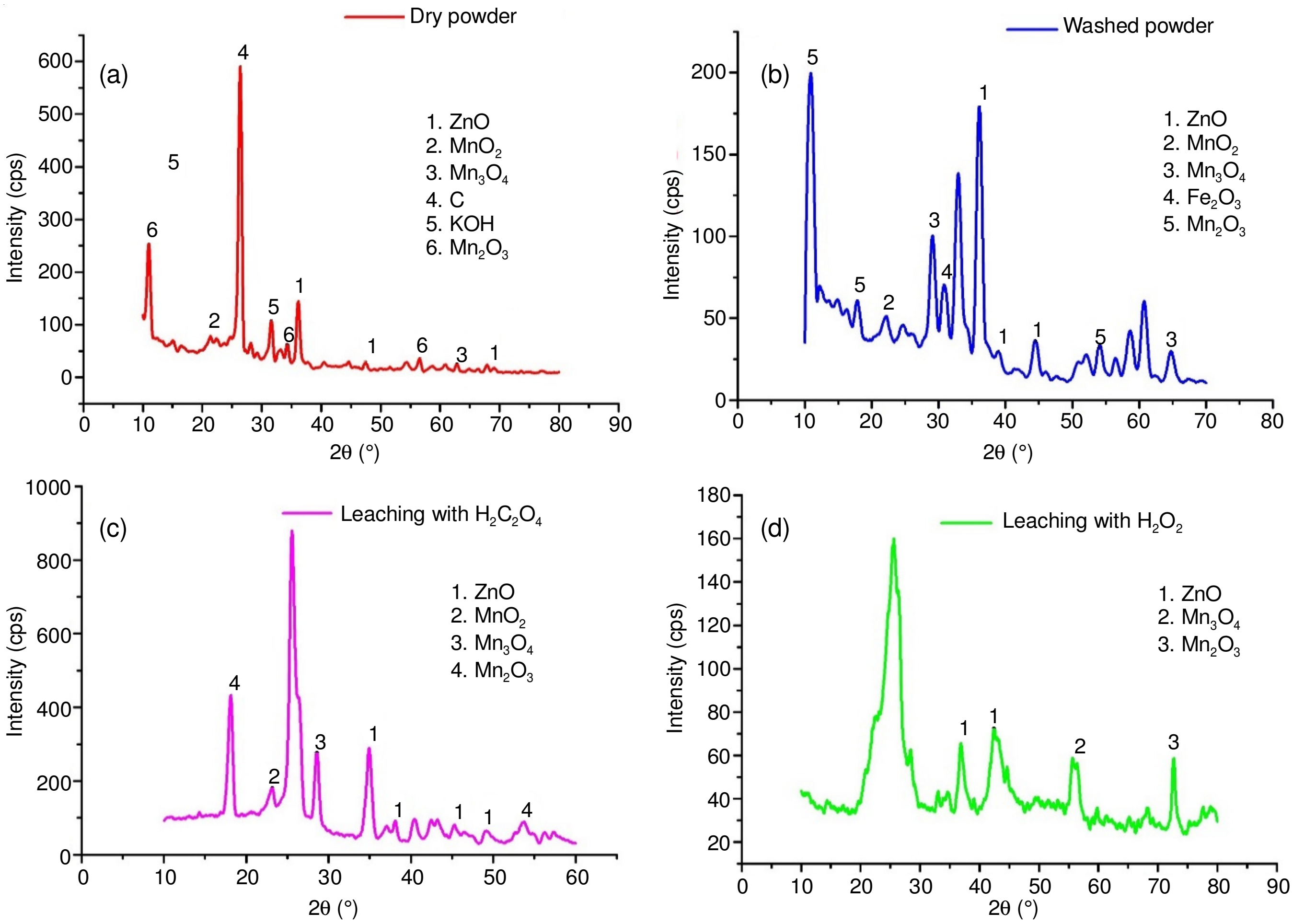

Fig. 5. XRD of spent batteries (a) dry powder, (b) washed powder, (c) leaching with $H_2C_2O_4$ (d) Leaching with H_2O_2

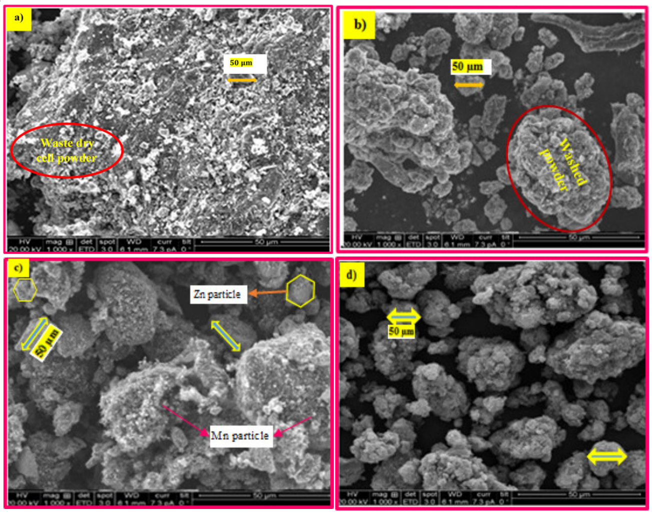

Fig. 6. SEM images of spent batteries (a) dry powder, (b) washed powder, (c) leaching with $H_2C_2O_4$ (d) leaching with H_2O_2

of the oxide as determined by XRD shown previously, appears as a mixture of manganese oxides (MnO_2, Mn_2O_3 and Mn_3O_4) thus confirming the results reported above. Impurities coming from other components of leaching solutions are not identified. It shows that manganese and oxygen contents were detected indicating the presence of large amount of manganese hydroxide.

Electrochemical studies

Cyclic voltammetry studies: Electrochemical activity of manganese oxide can be assessed by cyclic voltammetry (CV). The solid sample was kept at 200 °C for 1 h in oven to yield manganese dioxide. The MnO_2 electrode was prepared by mixing 15 wt. % of MnO_2 powder with 75 wt. % of graphite and using 0.25 g of silicone oil as binder. The gained sample analyzed by CHI604E work station was used for all electrochemical measurements. An electrochemical measurement involves three electrode system having working electrode, Ag/AgCl reference electrode and a platinum wire as counter electrode.

Cyclic voltammetry studies were performed in potential between 0 to -1 V at 10 mV scan rate and different scan rates from 10 to 50 mV's using 0.5 M NaCl, 0.5 M KCl, 0.5 M NaOH and 0.5 M Na_2SO_4 electrolyte as shown in the Fig. 9a to 9e. Cyclic voltammetry showed that the electrochemical reversibility of MnO_2 was increased using 0.5 M NaOH compared to other electrolyte due to the influence of scan rate. As the scan rate increases, the cyclic voltammetry differs from the ideal capacitive performance. This is because of redox reactions depends on the insertion-deinsertion of the protons from the electrolyte. At sluggish scan rates, the dispersion of ions from the electrolyte can upgrading access to just about all presented pores on the electrode surface, leading to a whole

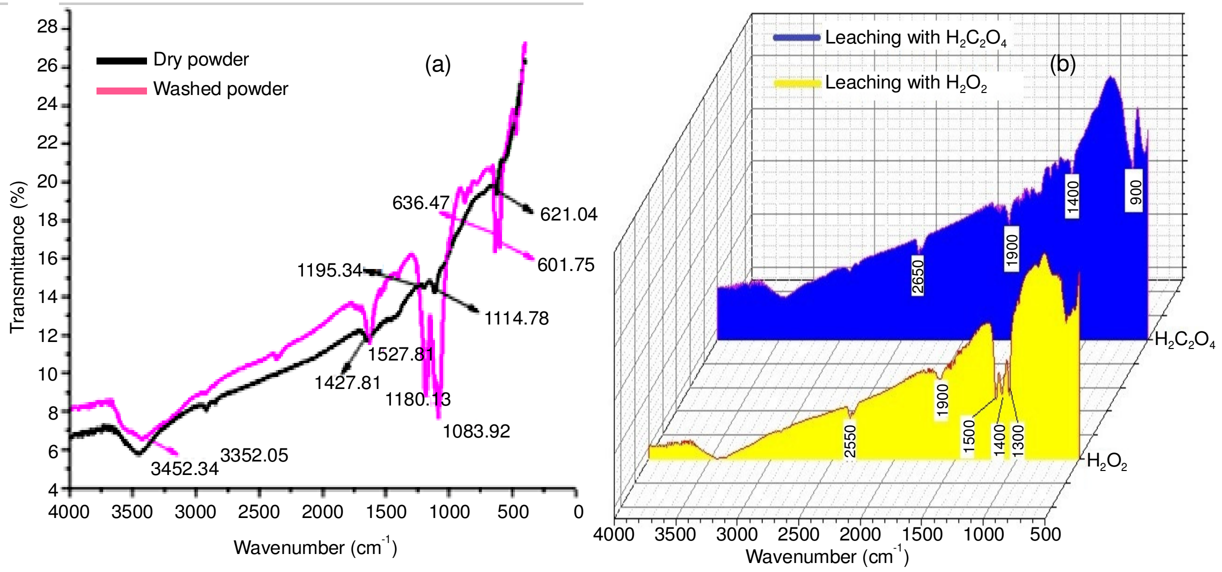

Fig. 7. FTIR spectrum of (a) dry and washed powder (b) leaching with $H_2C_2O_4$ and H_2O_2

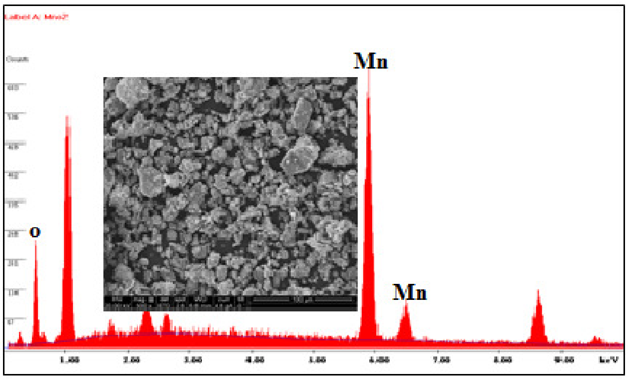

Fig. 8. EDAX/SEM images of recovered MnO_2 from dry cells

insertion reaction. Smaller the quantity of E_O-E_R displays superior reversibility of the electrode, Table-6 shows the reversibility [26,27] of electrode in 0.5 M NaOH is suitably more compared to lasting electrodes in 0.5 M NaOH electrolyte.

TABLE-6
OXIDATION POTENTIAL (E_O) AND REDUCTION POTENTIAL (E_R) OF DIFFERENT ELECTROLYTES

Electrolytes	E_a (V)	E_c(V)	E_a-E_c
0.5 M KCl	0.6879	0.4591	0.2280
0.5 M NaCl	0.7211	0.4061	0.3150
0.5 MNaOH	0.3385	0.3336	0.0049
0.5 M Na_2SO_4	0.3331	0.3004	0.0327

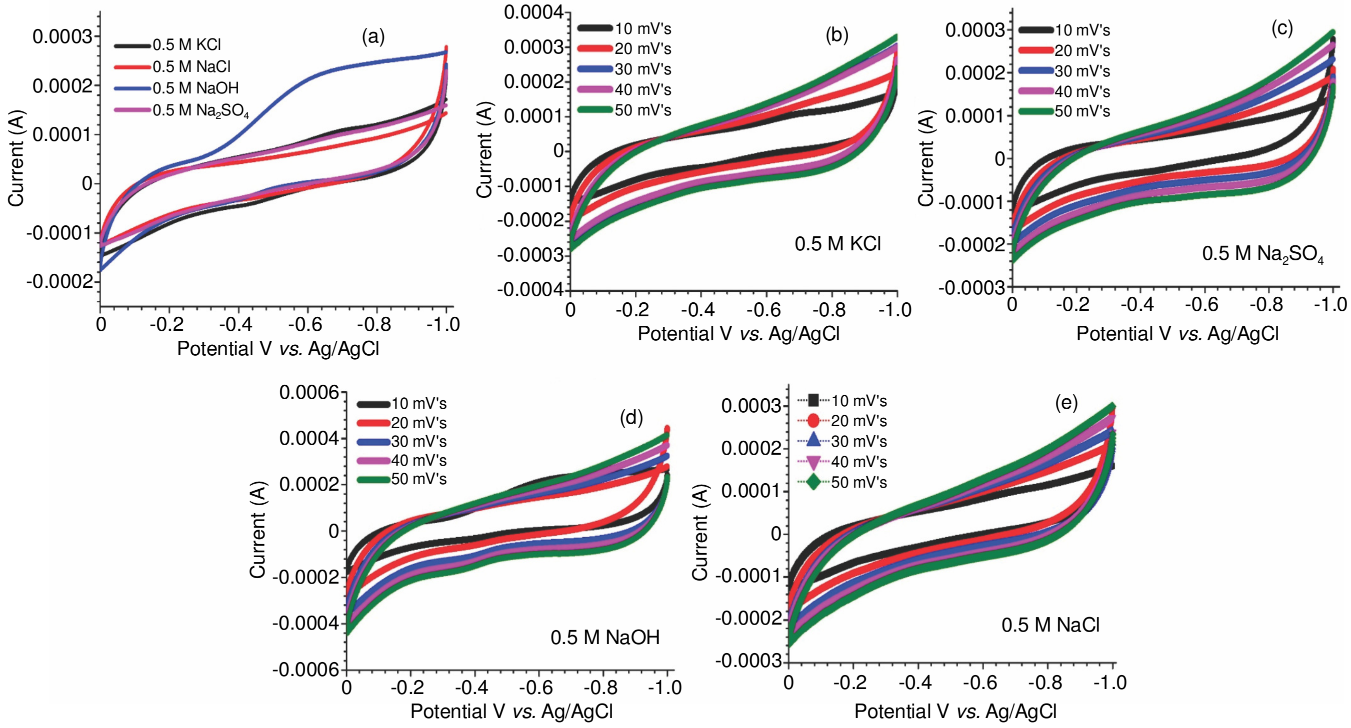

Fig. 9. (a) Cyclic voltammograms of MnO_2 using different electrolytes at 10 mV/s scan rate, (b) Using 0.5 M KCl, (c) 0.5 M Na_2SO_4, (d) Using 0.5 M NaOH, (e) Using 0.5 M NaCl

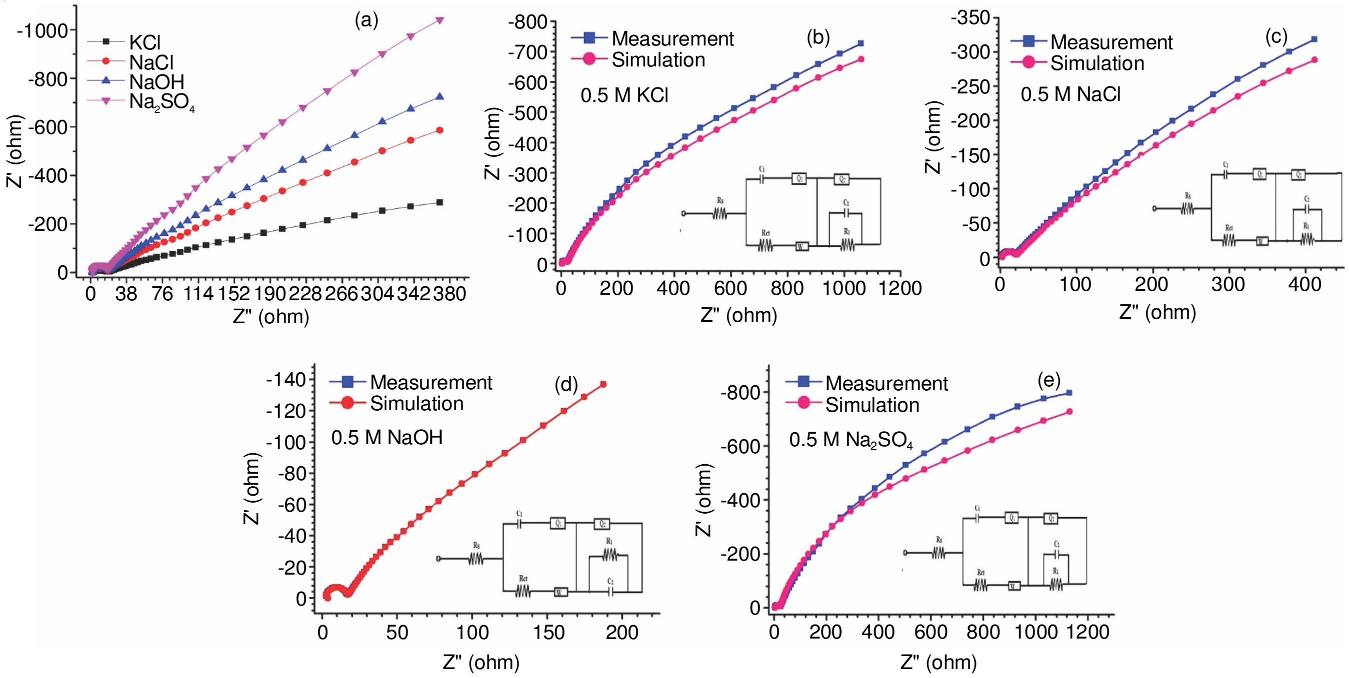

Fig. 10. (a) Nyquist plots of MnO_2 at different electrolytes and (b-e) Fitted Nyquist plots of MnO_2 at different electrolytes with equivalent circuits

Electrochemical impedance spectroscopy: The electrochemical impedance spectra (EIS) measurements were performed in order to further evaluate the electrochemical properties of MnO_2 as shown in Fig. 10a to 10e. Based on the experimental explanations, a common electrical equivalent circuit was suggested. It is seen that there is a good agreement between the measurement and simulated data. Experimental impedance data were best fitted to an electrical equivalent circuit (EEC) as shown in Fig. 10b to 10e. The Nyquist plot consists of a high frequency intercept on the real axis corresponding to the, ohmic resistance (R_s) of the capacitor, which is contributed by electronic resistances of the current collector leads to electrode material and a semicircle corresponding to parallel combination of charge transfer resistance (R_{ct}), double-layer capacitance (Cd_l) and finally, a linear region at low frequency range. Fig. 10a shows the low frequency region, the impedance plot increases sharply and tends to become vertical lines, which are the characteristics of pure capacitive behaviour. At the high frequencies, it is apparent that the values of R_s and R_{ct} gradually decrease with decreasing Warburg impedance [28,29]. This result is partially caused by the conductivity of the sample. It can be clearly found that the sample using 0.5 M NaOH has lowest R_{ct} and capacitance among all the electrolytes, Indicating better conductivity and confirmed that the charge transfer resistance and capacitive behaviour is faster and the results are shown in Table-7.

TABLE-7
CHARGE TRANSFER RESISTANCE AND CAPACITANCE VALUES OF DIFFERENT ELECTROLYTES OBTAINED FROM FITTED EIS CIRCUIT

Electrolytes	R_{ct} (ohm)	C(F) × 10^{-5}
0.5 M KCl	15.49	0.01706
0.5 M NaCl	16.66	0.01552
0.5 M NaOH	13.66	0.01945
0.5 M Na_2SO_4	16.74	0.01629

Conclusion

A hydrometallurgical method was used to separate Zn and Mn from spent alkaline batteries.

The presence of leaching agents increases the extraction of Zn and Mn simultaneously. By using oxalic acid and hydrogen peroxide as a leachants for the recovery from Zn and Mn spent dry cell batteries at 90 °C showed 99.25, 86.03 and 98.8, 81.56 %, respectively. Effect of H_2SO_4 concentration on Zn and Mn leaching is significant. From XRD spectra, zinc oxide and manganese oxides (Mn_2O_3, Mn_3O_4 and MnO_2) were the main components in all the spectra. The electrochemical activity of recovering MnO_2 from spent dry cell batteries improved the better electrochemical reversibility, Charge transfer resistance and capacitive performance of the MnO_2 using 0.5 M NaOH electrolyte and impedance measurements suggest that the charge-transfer resistance gradually first increases and thereafter decreases.

ACKNOWLEDGEMENTS

One of the author (MM) is grateful to University Grants Commission (UGC), New Delhi and Rajiv Gandhi National fellowship, letter no F.14-34/2011(cpp-II), dated 11-01-2013 for the finance assistance to complete the research work.

REFERENCES

1. G. Senanayake, S.M. Shin, A. Senaputra, A. Winn, D. Pugaev, J. Avraamides, J.S. Sohn and D.J. Kim, *Hydrometallurgy*, **105**, 36 (2010); https://doi.org/10.1016/j.hydromet.2010.07.004.
2. E. Sayilgan, T. Kukrer, F. Ferella, A. Akcil, F. Veglio and M. Kitis, *Hydrometallurgy*, **97**, 73 (2009); https://doi.org/10.1016/j.hydromet.2009.01.004.
3. G. Belardi, P. Ballirano, M. Ferrini, R. Lavecchia, F. Medici, L. Piga and A. Scoppettuolo, *Thermochim. Acta*, **526**, 169 (2011); https://doi.org/10.1016/j.tca.2011.09.012.
4. A. Sobianowska-Turek, W. Szczepaniak and M. Zablocka-Malicka, *J. Power Sources*, **270**, 668 (2014); https://doi.org/10.1016/j.jpowsour.2014.07.136.

5. A.A. Baba, A.F. Adekola and R.B. Bale, *J. Power Sources*, **171**, 838 (2009); https://doi.org/10.1016/j.jhazmat.2009.06.068.
6. F. Veglio, I. Volpe, M. Trifoni and L. Toro, *Ind. Eng. Chem. Res.*, **39**, 2947 (2000); https://doi.org/10.1021/ie990841i.
7. F. Veglio and L. Toro, *Hydrometallurgy*, **36**, 215 (1994); https://doi.org/10.1016/0304-386X(94)90007-8.
8. X. Tian, X. Wen, C. Yang, Y. Liang, Z. Pi and Y. Wang, *Hydrometallurgy*, **100**, 157 (2010); https://doi.org/10.1016/j.hydromet.2009.11.008.
9. W. Zhang and C.Y. Cheng, *Hydrometallurgy*, **89**, 160 (2007); https://doi.org/10.1016/j.hydromet.2007.08.009.
10. E. Sayilgan, T. Kukrer, N.O. Yigit, G. Civelekoglu and M. Kitis, *J. Hazard. Mater.*, **173**, 137 (2010); https://doi.org/10.1016/j.jhazmat.2009.08.063.
11. K. Maya and S. Kursunoglu, in eds.: L. Zhang, J. A. Pomykala and A. Ciftja, Dissolution of Mixed Zinc-Carbon and Alkaline Battery Powders in Sulphuric Acid Using Ascorbic/Oxalic Acid as a Reductant, Presented in EPD Congress 2012, John Wiley & Sons, Inc., Hoboken, NJ, USA (2012); https://doi.org/10.1002/9781118359341.ch32.
12. S. Kursunoglu and M. Kaya, *Asian J. Chem.*, **25**, 1975 (2013); https://doi.org/10.14233/ajchem.2013.132558.
13. S. Frohlich and D. Sewing, *J. Power Sources*, **57**, 27 (1995); https://doi.org/10.1016/0378-7753(95)02234-1.
14. A. Serstevens, Method for Recycling and Treating of Salt and Alkaline Batteries, European Patent EP1148571 (2009).
15. L. Toro, F. Veglio, F. Beolchini, F. Pagnanelli, Z. Mariachiara and F. Giuliana, Process and Plant for the Treatment of Run-Down Batteries, European Patent EP 1684,369 (2006).
16. C.C.B. Martha de Souza, D.C. de Oliveira and J.A.S. Tenório, *J. Power Sources*, **103**, 120 (2001); https://doi.org/10.1016/S0378-7753(01)00850-3.
17. F. Ferella, I. De Michelis, F. Veglio, F. Beolchini, E. Karakaya and M. Kitis, Recycling of Spent Alkaline a Zinc-Carbon Batteries for Zinc and Manganese Secondary Production, 2nd International Conference. of Advances in Mineral Resources Management and Environmental Geotechnology, Hania, Crete, Greece, 25-27 September (2006).
18. C.C.B.M. De Souza and J.A.S. Tenorio, *J. Power Sources*, **136**, 191 (2004); https://doi.org/10.1016/j.jpowsour.2004.05.019.
19. F. Veglio and L. Toro, *Int. J. Miner. Process.*, **40**, 257 (1994); https://doi.org/10.1016/0301-7516(94)90047-7.
20. G.M. Yavorskaya, V.A. Arsentev, V.L. Kucher and O.V. Kovaleva, Redox Leaching of Manganese from Oxide Feed Materials, SU Patent No. 1733492 (1992).
21. W. Zhang and C.Y. Cheng, *Hydrometallurgy*, **89**, 137 (2007); https://doi.org/10.1016/j.hydromet.2007.08.010.
22. A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum and M.B. Mansur, *J. Power Sources*, **115**, 367 (2003); https://doi.org/10.1016/S0378-7753(03)00025-9.
23. M. Buzatu, S. Săceanu, M.I. Petrescu, G.V. Ghica and T. Buzatu, *J. Power Sources*, **247**, 612 (2014); https://doi.org/10.1016/j.jpowsour.2013.09.001.
24. P. Macolino, A.L. Manci, I.D. Michelis, M.S. Anton, P. Ilea and F. Veglio, *Acta Metal. Slov.*, **19**, 212 (2013); https://doi.org/10.12776/ams.v19i3.163.
25. R.N.G. Guerra, F. Pedrosa, F. Margarido and C.A. Nogueira, Metals Recovery from Spent Zn-MnO_2 Batteries by Hydrometallurgy, Cancun-Mexico, REWAS 2008, The Minerals, Metals & Material Society (TMS), (2008); https://doi.org/10.13140/2.1.3430.8801.
26. M. Mylarappa, V.V. Lakshmi, K.R. Vishnu Mahesh, H.P. Nagaswarupa and N. Raghavendra, *IOP Conf. Series: Mater. Sci. Eng.*, **149**, 012178 (2016); https://doi.org/10.1088/1757-899X/149/1/012178.
27. M. Mylarappa, V.V. Lakshmi, K.R. Vishnu Mahesh, H.P. Nagaswarupa, S.C. Prashantha, D.M.K. Siddeswara and N. Raghavendra, *Nanosystems: Phys. Chem. Math.*, **7**, 657 (2016); https://doi.org/10.17586/2220-8054-2016-7-4-657-661.
28. D.M.K. Siddeswara, K.R. Vishnu Mahesh, S.C. Sharma, M. Mylarappa, H. Nagabhushana, K.S. Ananthraju, H.P. Nagaswarupa, S.C. Prashantha, and N. Raghavendra, *Nanosystems: Phys. Chem. Math.*, **7**, 678 (2016); https://doi.org/10.17586/2220-8054-2016-7-4-678-682.
29. K.N. Shravana Kumara, H.P. Nagaswarupa, K.R. Vishnu Mahesh, S.C. Prashantha, M. Mylarappa and D.M.K. Siddeshwara, *Nanosystems: Phys. Chem. Math.*, **7**, 662 (2016) https://doi.org/10.17586/2220-8054-2016-7-4-662-666.