



Titanium Dioxide as a Cathode Material in a Dry Cell

Duncan ALOKO and Eyitayo Amos AFOLABI

Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria
alokoduncan@yahoo.com, elizamos2001@yahoo.com

Abstract

Titanium dioxide was proposed as an alternative cathode material in place of Manganese (IV) oxide. TiO_2 was found to be highly polarized when in an electric field and its surface area of adsorption of solution determined to be $1070.32 \text{ m}^2/\text{g}$. The adsorption of alkaline anions (i.e. SO_4^{2-} , NO_3^- , Cl^- and Br^-) were investigated. The anions were adsorbed between the layers of the cathode material thereby altering its surface texture for a better performance. Increase in concentration of the anions solution enhances greater electric surface charge. Thus, sulphate ion is having the best result as compared to other anions because of its highest electric charge and adsorption at 1M concentration of solution. This is in agreement with the relative position of ions in the electrochemical series in the decreasing order of electro- negativity as well as in the increasing order of preference for discharge.

Keywords

Dry cell; Cathode Materials; Depolarization; Potentiometric Titration.

Introduction

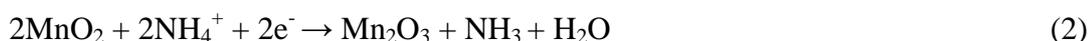
There seems to be a correlation between electricity provision and life expectancy. Consequently, electricity provision is probably one of the most parameters of modern life. Throughout the developing world, electricity is a necessity for economic growth. With

continuous developments in the power industry, it is essential that newer and cheaper source of energy are found to replace conventional energy sources. In 1866, Leclanche dry cell was invented and is an offshoot of the present day dry cells especially the zinc- carbon dry cell.

The operating voltage for a dry cell is usually between 0.9 and 1.4 volt. The electrochemical system of a leclanche dry cell with salt electrolyte is given as:



At Cathode



At Anode



Polarization effect and local action are two defects of dry cells. These defects slowly down the effectiveness of dry cell and shorten its longevity hence the need for an effective depolarizer in order to minimize or completely eliminate polarization of the carbon electrode, thus preserving the life of the cell and enhance its longevity.



The effect of MnO_2 as a depolarizer by adsorbing the hydrogen gas formed at the positive carbon electrode has not completely eradicated the evolution of hydrogen gas. Several attempts have been made to correct the polarization effect as well as to improve the capacity of dry cell. Bockris (1972) included zinc Chloride in electrolyte with the aim of reducing polarization process. Eveready (1988) suggested the inclusion of Calcium Chloride in the electrolyte to improve on the ionic conductivity of the electrolyte. [7, 8, 9]

This study employed TiO_2 as alternative depolarizer and determined the effect of blending TiO_2 with alkaline anions to improve its polarization performance. The uniqueness of TiO_2 properties makes it an effective depolarizer. These include a relatively large surface area for adsorption of molecules, its ability to undergo a reduction reaction with H_2 to give Ti_3O_5 and the ability to be highly polarized when an electric field is applied to a crystal of Ti^{4+} . Also, TiO_2 is found to be chemically inert, has a high melting point and the white pigment of TiO_2 has an exception high refractive index in the visible region of the spectrum. [1, 2, 5]

Addition of various anions to the active mass of the electrode is aimed at preventing the electrode crumbling, suppressing dendritic growth and modification of electrolytes and to increase the depolarizer effectiveness. The effect of anions is observed in alteration of surface texture thereby minimizes ionic impurities and enhances the electrode life span

Methodology

Determination of Physical Properties of TiO₂

The physical properties of TiO₂ that were determined include texture, colour, and solubility in water. [5]

Determination of Density of TiO₂

A density bottle was washed, cleansed, dried and weighed empty. The mass was then recorded. The density bottle was filled with some quantity of TiO₂ and then weighed and the mass recorded. Deionised water was added to the content of the bottle until it was filled, weighed and the mass recorded. Then the bottle was emptied, washed, cleaned and dried. It was filled with deionized water only, weighed and the new mass recorded. [5]

Procedure for Determining the Specific Surface Area of TiO₂ Adsorption

Clean seven well labeled flat bottomed flasks cleaned with glass stopper tops. Put 1 g of TiO₂ sample into six of the flat - bottomed flasks and then add 100 ml of acetic acid solution each of concentration 0.015M, 0.03M, 0.06M, 0.09M, 0.12M, and 0.15M to their separate flask. The seventh flask was without 1g of TiO₂ sample but 100 ml of 0.3M acetic acid was placed in it and this sample serve as a control. The seven flasks were tightly stoppered with plastic or rubber cork and each flask were shaken periodically for 30 minutes, and then allowed to stand in a thermostat bath at 25°C for 24 hours. When equilibrium has been reached (after 24 hours) the solutions were filtered into clean conical flask, but the first 10ml of the filtrate for each of the mixtures was discarded as a precaution against adsorption of the acid by the filter paper.

Two 25ml portions of the filtrate (aliquots) were titrated against 0.1M Sodium hydroxide solution using phenolphthalein as an indicator. Also, as a side reaction, an extra

sample containing 1g TiO_2 was put into deionized water, treated and filtered with two 25 ml filtrate taken and titrated against 0.1M Sodium hydroxide separately and the end point observed. The same procedure was repeated for the remaining concentrations of the acetic acid solutions.

From the titre values, the new concentrations of the acetic acid solutions were calculated, thus, the numbers of moles present before and after adsorption were similarly calculated and the difference obtained. These values were used to calculate values for C/N and hence a plot of C/N against C was drawn. The slope of the straight line obtained, was calculated and used for the calculation of the adsorption area of TiO_2 . [3, 4 &10]

Potentiometric Titration Procedures for the Determination of Adsorption of the Anions by TiO_2

To a clean dry 100ml beaker, a little of 1M sodium bromide was measured with a 50ml pipette and transferred into the beaker, and a magnetic follower placed inside to provide a continuous stirring. A reference electrode and an indicator connected to a pH meter were hanged into the solution in the beaker. Then a nitrogen gas jet regulated by a gauge from the nitrogen gas cylinder was additionally inserted into the solution. Furthermore a burette filled with 0.1M trioxonitrate (v) acid solution was also placed such that its tip was directly pointed to the solution in the 100ml beaker. When all the instruments have been neatly arranged, the magnetic stirrer was switched on and the nitrogen gas regulator opened to provide a continuous gas jetting into the solution by bubbling.

After the pH meter was stabilized and the initial pH reading without the 0.1M solution of trioxonitrate (v) acid was noted. 0.50ml of titrants (acid) was subsequently added from the burette and the pH reading noted for every 2 minutes after each addition (i. e when the indicator electrode had reached a constant value). The 0.50ml increment and the corresponding pH reading were noted for a total of 10.00ml addition when no significant change was observed in the reading. At the end, both the magnetic stirrer and the pH meter were switched off and the solution mixture disposed.

Similarly, another 50ml of the 1M sodium bromide solution was pipette into the beaker (after it has been washed and rinsed with the solution) and 2g of TiO_2 added. The magnetic follower was then inserted the beaker and the whole set- up was arranged after stabilizing the pH meter with distilled water. The same procedure was repeated for a total of



10.00ml of 0.50ml addition of the 0.1M trioxonitrate (v) acid for 0.1M, 0.01M, and 0.001M of the NaBr. The adsorption and surface electric charge were calculated.

The pH versus the volume of the titrant obtained was plotted for both the adsorption of anion without and with TiO₂ on the same graph. At a given pH, the difference in volume (ΔV) between the two graphs was used to calculate adsorption. The value of absorption (θ) is calculated using Kokarev's formula (Kokarev, et.al, 1988):

$$\theta = \frac{\Delta vc}{s1000} \left(\frac{\text{Mole}}{\text{cm}^2} \right) \quad (6)$$

where c = concentration of HNO₃ in mole / litre and s = surface area (m² /g).

The electric surface charge of chloride ion adsorption, Y, in coulomb/ cm² is given by:

$$Y = nF\theta \quad (7)$$

n= absolute number of ionic charge and F = Faraday's constant.

The same experimental procedure was repeated for different concentrations (1M, 0.1M, 0.01 and 0.001M) of NaCl, NaNO₃ and NaSO₄. [3, 4&10]

Results

The data obtained from the experiments were tabulated in Table 1 and 2. In Fig.1, a graph of Concentration per moles against concentration of the adsorbate was obtained, while Figures 2 to 5 shows the variation of the pH against changes in volume of the 0.1M of HNO₃ for different anions. Figures 6 to 9 gives the variation of the effect of concentration on electric charge and adsorption of TiO₂.

Table 1. Physical Properties of TiO₂ Sample

Property	
Texture	Powdery
Color	White
Solubility	Soluble in H ₂ O
Density	1.55g/cm ³
Operating Temperature	30°C

Table 2. Titration of 0.1M NaOH against Acetic acid

Initial Conc. of Acetic acid	Vol. of Acetic acid (ml)	Average vol. of NaOH (ml)	Initial Conc. of Acetic acid (M)	Final Conc. of Acetic acid (M)	Initial number of moles (N_1)	Final number of moles (N_2)	Number of moles (N) $N = N_1 - N_2$	C/N
0.15	25	47.08	0.15 + 1g TiO_2	0.1883	0.015	$4.7 \cdot 10^{-3}$	$1.03 \cdot 10^{-2}$	18.28
0.12	25	40.90	0.12 + 1g TiO_2	0.1636	0.012	$4.1 \cdot 10^{-3}$	$7.9 \cdot 10^{-3}$	20.71
0.09	25	30.53	0.09 + 1g TiO_2	0.1221	0.009	$3.1 \cdot 10^{-3}$	$5.9 \cdot 10^{-3}$	20.69
0.06	25	20.25	0.06 + 1g TiO_2	0.081	0.006	$2.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	20.25
0.03	25	12.50	0.03 + 1g TiO_2	0.050	0.003			21
0.015	25	7.65	0.015 + 1g TiO_2	0.0306	0.0015	$8.0 \cdot 10^{-4}$	$7.00 \cdot 10^{-4}$	43.71
0.03	25	0.35	0.15 + 0.03M acid	0.0014	0.0075	$3.5 \cdot 10^{-5}$	$7.15 \cdot 10^{-4}$	40.00

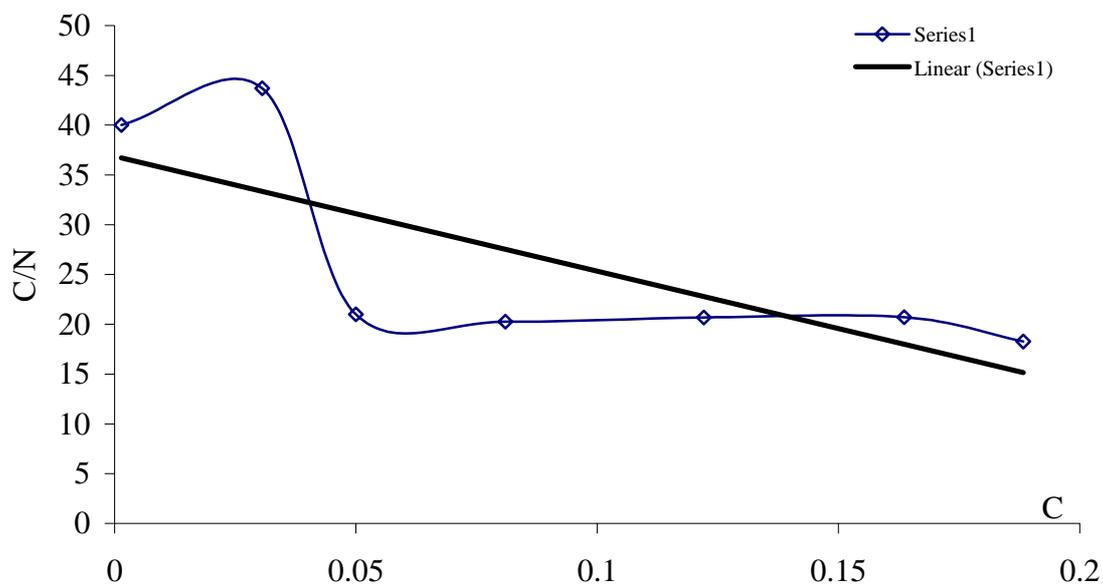


Figure 1. Graph of C/N against C

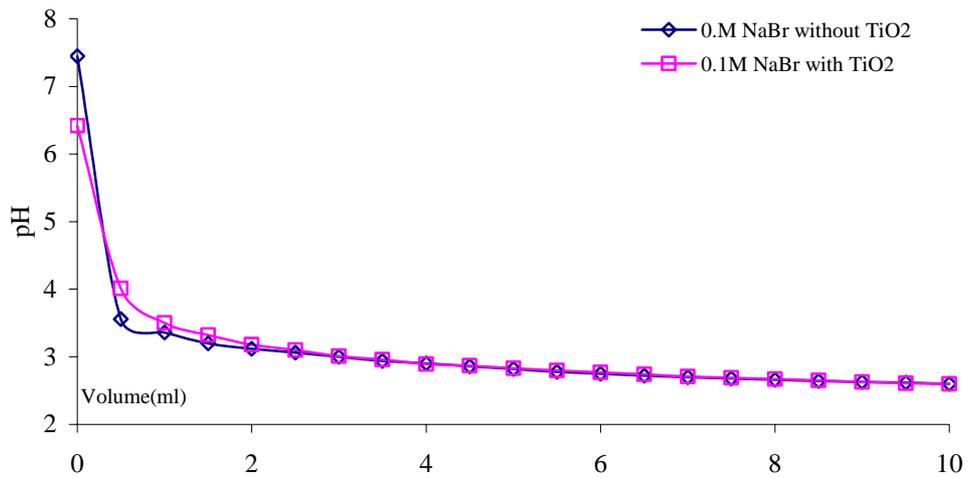


Figure 2. Graph of pH against Volume for Adsorption of Bromide Ion

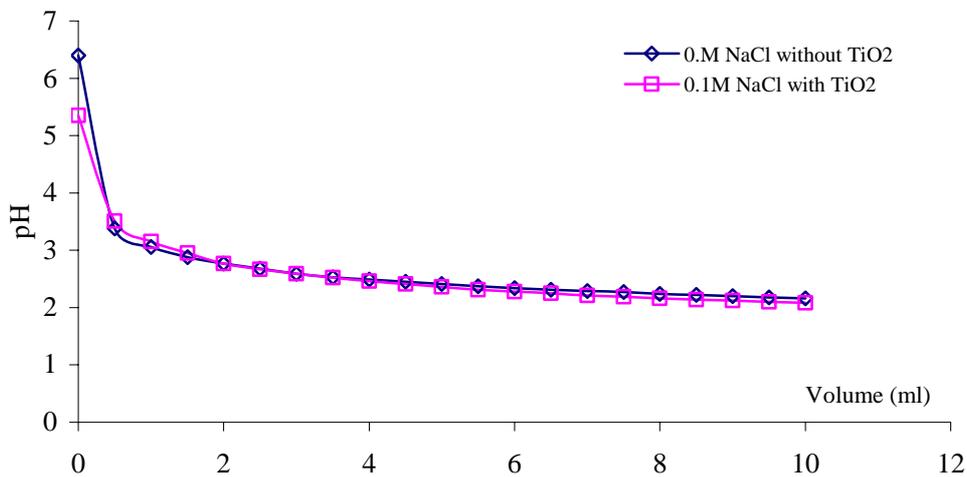


Figure 3. Graph of pH of 0.1M NaCl against Volume of 0.1M HNO₃

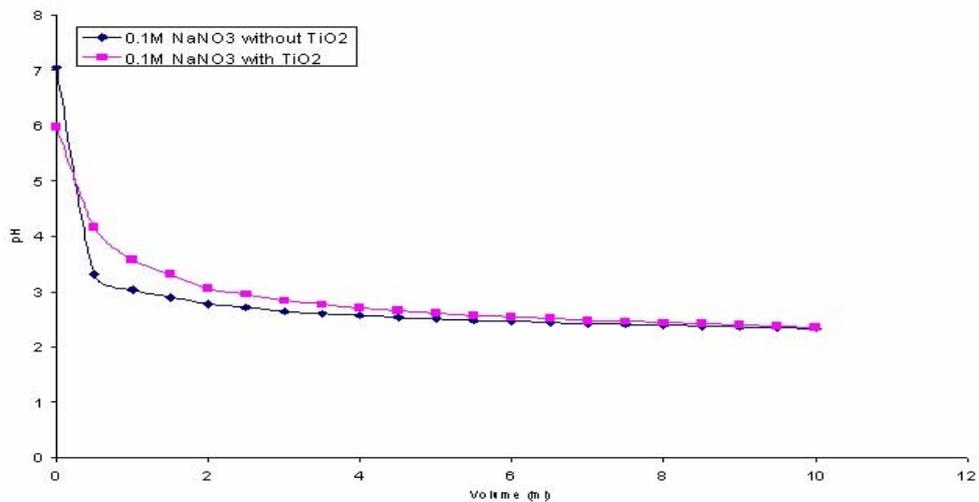


Figure 4. Graph for the Adsorption of Nitrate ion

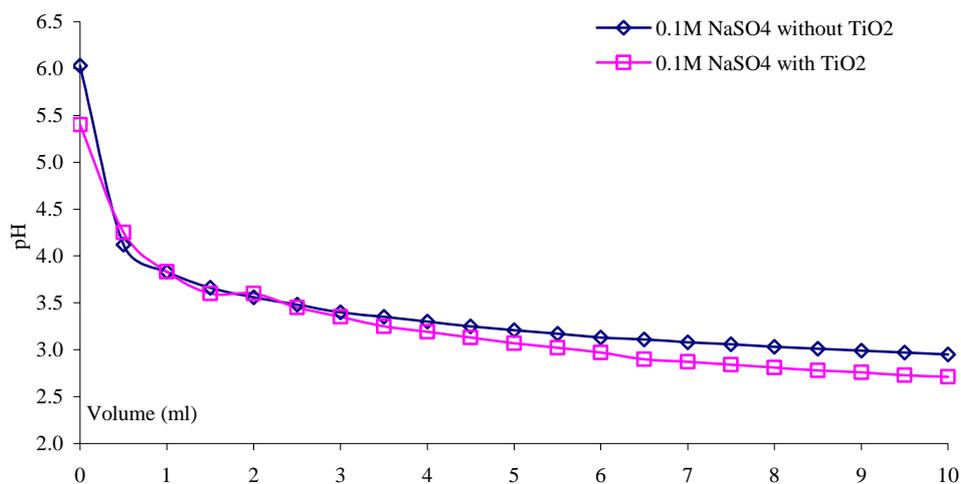


Figure 5. Graph for the Adsorption of Sulphate Ion

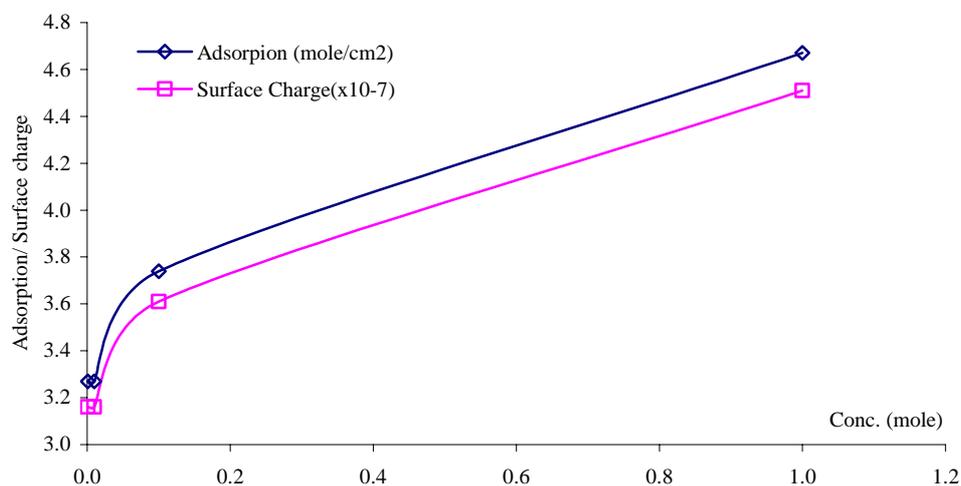


Figure6. Effect of Concentration on Electric charge and Adsorption of Bromide Ion

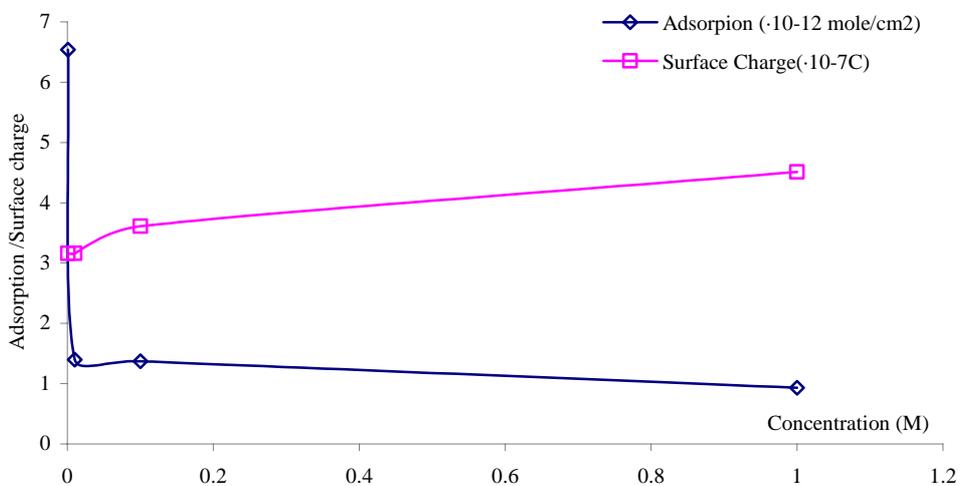


Figure 7. Effect of Concentration on the Electric charge and Adsorption of Chloride Ion

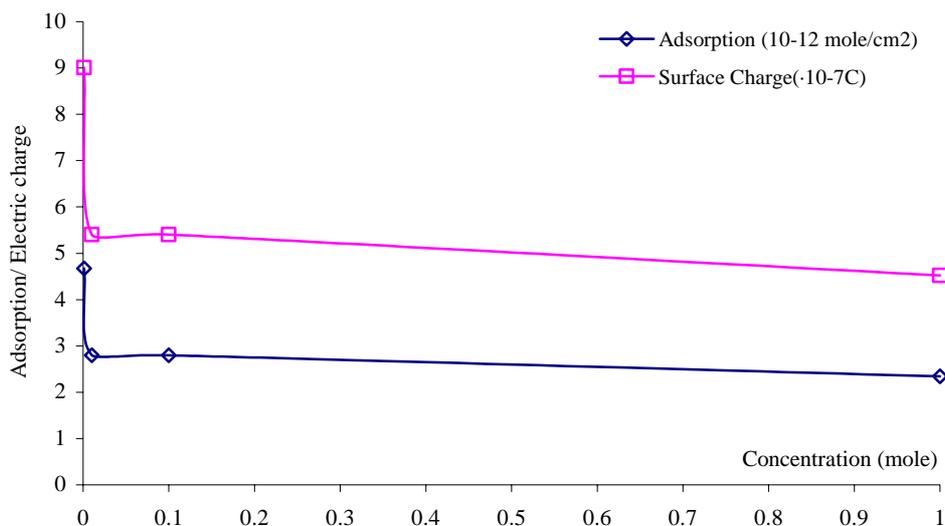


Figure 8. Effect of Concentration on the Electric Charge and Adsorption of Sulphate (VI) Ion

Discussion of results

Calculation of Adsorption Specific area

$$\text{Specific area of Adsorption, } A = N_m N_d \& \times 10^{-20}$$

where

- N_m = Number of moles per gram require to form a monolayer
- N_d = Avogadro constant, 6.023×10^{23}
- $\&$ = Adsorption area of Acetic acid = 21
- From Fig.1, the slope of the plot of C/N against C ($1/N_m$) was found to be 118.18

On Substitution into Equation (1), the specific area of adsorption was calculated to be $1070.35 \text{ m}^2/\text{g}$

pH Responses during Titration

In the potentiometric titration, as more volume of titrants (HNO_3) was added to the solution, the pH value of the solution tends toward acidity. Also observed was that at any given equal volume of titrants added, the pH value of the solution with TiO_2 was almost higher than those without TiO_2 . This was as a result of the anions adsorbed whenever there is TiO_2 in the solution, resulting in lesser ions and consequently lowers acidity of the solution.

But in the case of the solution without TiO_2 , the whole ions were still present in the solution and therefore higher acidity.

From Figure 2 to 5, it was observed that the change in pH with successive addition of titrants to the solution decreases as titration progresses. This was true for both solutions with and without TiO_2 . Therefore, as the absorption of the anions progresses, the number of sites left for further adsorption decreases with time. Hence, the change in pH value decreases. This is in agreement with the fact if all the TiO_2 are covered by the adsorbed molecules (complete mono-layer adsorption), then further titrants will yield no change in pH between solutions with and without TiO_2 .

Effect of Concentration on Surface charge

The surface charge of Sulphate (VI) ion increases with an increase in concentration of the solution (see Fig. 9). While, the surface charge of Bromide ion decreases with an increase in concentration of its solution as observes in Fig. 8. Fig. 7 shows a hypothetical relation, in which the highest surface charge was at 0.1 M NO_3^- solutions while the least surface charge value was at a 1M concentration of NO_3^- solution. Also, Fig. 6 gives a hypothetical relation for adsorption of chloride ion which has the highest surface charge value at 0.01M solution and the least surface charge obtained at 1M solution (see Table 3).

Table 3. Concentration and order of Surface Charge

Concentration	Reducing order of Surface Charge
1M	$\text{SO}_4^{2-} > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$
0.1M	$\text{NO}_3^- > \text{Br}^- > \text{SO}_4^{2-} > \text{Cl}^-$
0.01M	$\text{Cl}^- > \text{Br}^- > \text{SO}_4^{2-} > \text{NO}_3^-$
0.001M	$\text{Br}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$
Thus	$\text{Br}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$

This implies that in the electrochemical series, less electronegative ion is discharge in preference to another which is more electronegative as the former losses electrons more readily.

Effect of the Anions on the Adsorption

The anions additives are believed to be adsorbed between layers of the cathode material. Thus, the effect of the anions is seen in the alteration of surface texture. At 1M concentration,



solution of SO_4^{2-} ion has the highest adsorption while that of NO_3^- , Cl^- and Br^- were at 0.1M, 0.01M and 0.001M respectively.

Conclusion

TiO_2 is a good polarizer and can be used as an alternative cathode material depolarizer in place of MnO_2 in leclanche dry cell. Its adsorption surface area was calculated to $1070.35\text{m}^2/\text{g}$. Increase in concentration of the anions solution enhances greater electric surface charge with sulphate ion having the highest electric charge and adsorption at 1M concentration of solution. This is in agreement with the relative position of ions in the electrochemical series in the decreasing of electro negativity as well as in the increasing order of preference for discharge.

Recommendations

- (1) The work on cations such as K^+ and Li^+ should be consider and their positive influence on the cathode material carefully investigated.
- (2) The preparation of all solution concentration should be carefully done from their base stock. This eliminates the error in determination and use of inaccurate solution.

Reference

1. Ababio O.Y, *New School Chemistry*, African - FEP Publishers Limited, New Edition, Singapore, 1990.
2. Adeyemi O, *Collection on Dry Cell*, Project Notebook (Unpublished work) F. U. T Minna, Nigeria, 2000.
3. Afene A .G., *Study on the Adsorption of Alkaline Anions on Manganese IV Oxide used in Dry Cell*, B. Eng. Thesis, F. U. T Minna, Niger state, Nigeria, 1998.

4. Braun R.D, *Introduction to Chemical Analysis*, McGraw- Hill International Editions, Singapore, 1983.
5. Darby R.S and Leighton, J., *Titanium dioxide Pigment in the Modern in Organic Chemical Industry*, The Chemical Society, London, No. 31, 1977.
6. Hicks T.G , *Standard Handbook of Engineering Calculation*, Third Edition, McGraw Hill Inc, 1972.
7. Journal of Power Source, *The international Journal on the Science and Technology of Electrochemical Energy Systems*, July- August, '96, Vol.61 No 1, 2. Sept '96, Vol. 62, No.1, Nov. '96, Vol. 63, No1,
8. Perry R.H., Green D.W., *Chemical Engineers Handbook*, 6th Edition, Mc Graw - Hill book company, New York, 1984.
9. Parker S. P., *Concise Encyclopedia of Science and Technology*, Second Edition, Mc Graw - Hill Publication, New York, 1978.
10. Varma R., Selman J. R., *Techniques for Characterization of Electrodes and Electrochemical Processes*, John Wiley and Sons Inc, 780 p., 1991.