© March 2018 | IJIRT | Volume 4 Issue 10 | ISSN: 2349-6002

Electrodeposited Three Dimensional PB Nano Wire Anode for Thin Film Li-Ion Micro Batteries

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Abstract- **The Pb wire grown over anodic aluminium oxide template is used as anode for Li ion batteries. Thiswork entails porous template formation through double step electrochemical oxidation method optimized by design of experiment and Tafel polarization. The X-ray diffraction results of different anodized specimens show amorphous alumina layer formation. The pores in alumina matrix and the filamentous outward projection of Pb wires are observed from micrographs. The initial discharge capacity of Pb wire and Pb planar thin film is observed to be around 830 and 618 mAh/g respectively. The 55thcycle capacity of Pb wire is observed to be around 485 mAh/g which is very high when compared to theoretical capacity of graphite anodes.**

Index Terms- **sputtering, electrodeposition, corrosion, energy storage and conversion, thin films.**

1. INTRODUCTION

Amongst the existing energy storage technologies Li ion battery technology is clearly emerging as front-runner due to its high energy density. However, it is quite interesting to note that the gravimetric capacities of state of art battery systems are trailing the expectation to meet the actual demand. In such scenario, many significant research contributions are emerging from the aspects of materials science, nano technology and battery design. Nevertheless, the extent of contribution on electrode materials are observed to be concentrated around cathode due to the limitation put forth by the cathode on gravimetric capacity of the batteries [1]. Hence concentrated efforts are needed to improve the performance of the anode materials which are responsible for reversible accommodation and release of Li ions in batteries. Among different anode materials [2–4], Co has received great deal of attention owing to its high theoretical capacity and low cost compared to graphite. However, the commercialization of Co based anodes is impeded by the virtue of their low columbic efficiency due to irreversible volume change upon lithium insertion and release [5]. Henceforth, the means to alleviate this volume expansion by tailoring the structure of the electrodes has received great attention.

In order to develop nano structured electrode many methods have been established and among them the template assisted growth of electrode is more advantageous due to the feasibility to control the size and spatial arrangement of the electrodes [6]. Hence in this manuscript the process to develop Pb wires in anodic aluminium oxide (AAO) template by double step electrochemical oxidation process is discussed. The extent of template formation has been comprehensively investigated by Tafel polarization studies and has been proved to be a facile way to analyze the tem-plate formation process. To the best of our knowledge, no such reports are available that utilize electrochemical method to analyze template formation. This manuscript also entails the structural properties of thin films of Al, aluminium oxide and morphological properties of AAO template, Co electrode and their corresponding battery performances.

2. EXPERIMENTAL

The aluminium thin films of approximate thick-ness 2.2 μm were sputter deposited from 2 inch aluminium target (purity 99.99%) over copper substrate of thickness 0.4 mm at room temperature and at 573 K respectively in high pure argon atmosphere (purity 99.9%). Prior to the deposition, the copper substrates were subjected to ultrasonic cleaning in triple distilled water for 30 min at room temperature and subsequently dried in vacuum at 373 K. The thickness of the

ELECTRODEPOSITED THREE DIMENSIONAL Pb NANO WIRE ANODE				
Tafel Polarization parameters				
Sample no.	Potential, V	Concentration, M	Inter electrode gap, cm	I, mA /cm2 Corr
1	5	0.5	1	2.226
2	20	0.5	1	2.226
3	5	3	1	2.377
4	20	3	1	2.444
5	5	0.5	3	2.487
6	20	0.5	3	2.380
7	5	3	3	2.380
8	20	3	3	2.439

deposits was analyzed ex-situ using Dektak stylus pro-filometer through step height measurement method. The aluminium thin films were subjected to anodization in different concentrations of H_2SO_4 solution ranging from 0.5 to 3 M and by applying different DC voltages ranging from 5 to 20 V. The optimum anodization process parameters were analyzed using 'Design of Experiment' (DoE) concept. DoE was adopted in this work to determine simultaneously the individual and interactive influence of many factors that affect the anodization process. Among the factors that influence the anodization process, three factors were chosen as most influential and they were(i) applied potential, (ii) concentration of electrolyte and (iii) inter electrode gap. For each factor two levels were chosen and based on alternate hypothesis, eight different experiments were carried out with process parameters as illustrated in table. The extent of Al_2O_3 layer formation was analyzed through Tafel polarization analysis in 1 M NaOH solution using CH 660A electrochemical workstation. For the Tafel polarization studies, the Al_2O_3 thin film, platinum wire and $Ag^+/AgCl$ were used as working electrode, counter electrode and reference electrode respectively. The corrosion current (Icorr) values actually corresponding to the corrosion of aluminium layer lying beneath the aluminium oxide layer was taken as the key indicator of anodization and the results were fed into the DoE analysis. The detailed mathematical equations involved in DoE analysis could be referred elsewhere [7] After anodization, the samples were subjected to etching in 1 M H_3PO_4 and 1 M H_3CrO_3 solution. After etching, the samples were subjected to anodization process again and which was referred to as second step anodization in 0.5 M H_2SO_4 solution at 20 V DC potential. After anodization, the samples were subjected to morphological analysis for possible template formation using Tescan LMU model scanning electron microscope. The template was subjected to zin-cating through immersion in a solution containingZnO (0.2 g/L), $NaNO_3$ (0.025 g/L) $C_4H_4KNaO_6$ (0.6 g/L), $NiCl_2$ (0.075 g/L), NaOH (40 g/L) for 30 minutes at room temperature [8]. The zincating process is mainly carried out to increase the surface conductivity of the aluminium layer and to prepare the aluminium surface to adhere to the metallic layers cathodically electrodeposited over them.The zincated AAO template and the copper substrate are subjected to Co electro deposition from a bath containing $PbSO_4$ (30 g/L); H_2SO_4 (100 mL/L)and tartaric acid (5 g/L) at 20 mA/cm2 current density for 10 minutes. The approximate loading of Co in AAO template and in copper substrate is maintained around 1 mg/cm2. The Co coated over copper substrate is referred to as planar Co electrode hereafter.The Co electrodeposited AAO template electrodes of 1 cm2 area were tested for battery performance against Li foil which was used as both reference and counter electrode. The battery assemblies were carried out in MBraun Unilab argon filled glove box and the electrolyte used was 1M $LiPF_6$ dissolved in mixture of 1 : 1 EC : DMC (wt %). The battery performances were tested at constant current mode (100 μA) using CH Electrochemical workstation.

3. RESULTS AND DISCUSSION

3.1. Electrochemical and DoE Analysis

The aluminium thin films deposited at 485 K are subjected to anodization as per the conditions provided in table and the Tafel polarization results of the resultant samples are presented in Fig. 1a. The values of Icorr calculated from the Fig. 1a are also tabulated in table. According to electrochemistry fundamentals, it is understood that lower Icorr means higher charge transfer resistance occurring due to surface passivation and hence from the table and Fig. 1a, it could be inferred that the anodization by applying 20 V in 0.5 M H_2SO_4 with 1 cm inter electrode gap has resulted

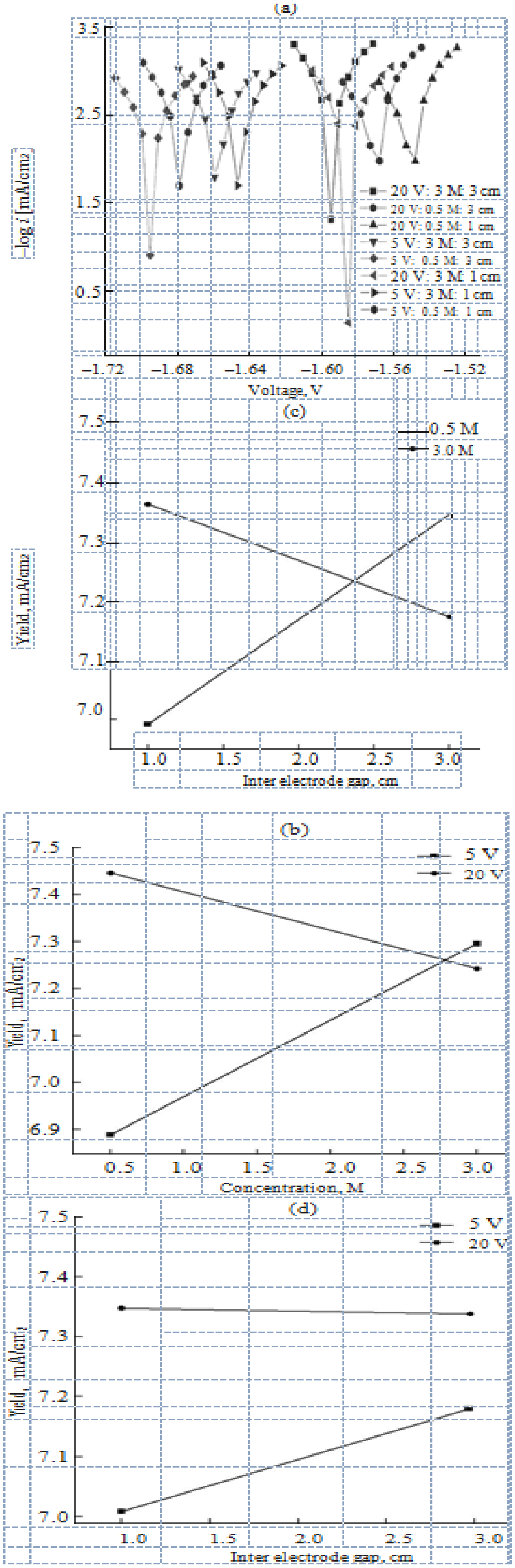


Fig.1. *(a) Tafel polarization plot for various conditions.(b) Interaction plot between concentration of the electrolyte and applied potential. (c) Interaction plot between inter electrode gap and concentration of the electrolyte. (d) Interaction plot between inter electrode gap and applied potential.*

low Icorr. On the other hand the higher Icorr synonymous to lower passivation is observed for the sample anodized by applying 5 V in 0.5 M H2SO4 with 3 cm inter electrode gap.

The DoE technique is adopted in this work and is used to determine simultaneously the individual and interactive effects of many factors that could affect the Icorr values. The interactions among the process parameters like applied potential & electrolyte concentration, applied potential & inter electrode gap and concentration & inter electrode gap are exemplified in Figs. 1b, 1c and 1d respectively. The interaction between applied potential and electrolyte concentration is identified to be higher. The maximum value

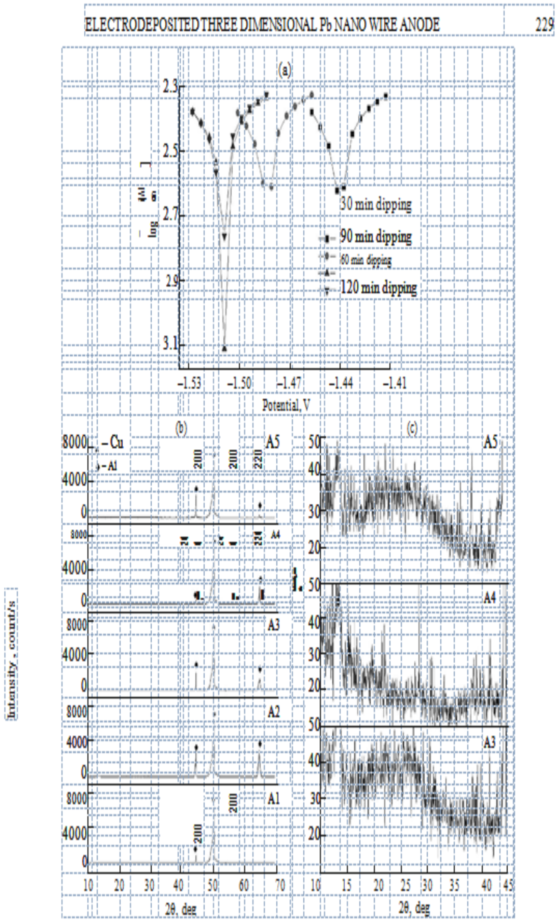
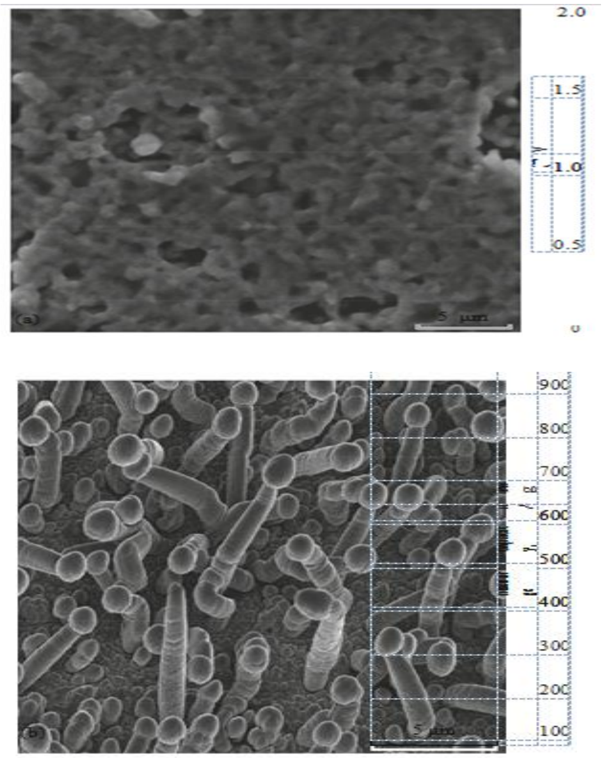


Fig. 2. (a) Tafel polarization plot for dipping process. (b) X-ray diffraction analysis. A1—as such deposited in Cu substrate, A2—deposited with 300°C substrate heater in Cu substrate, A3—after 30 min anodization process, A4—after 30 min etching process, A5—Double anodized sample. (c) X-ray diffraction analysis at lower two theta window, A3—after 30 min anodization process, A4—after 30 min etching process, A5—double anodized sample.

Corresponding to maximum surface passivation is observed to occur in the case of 20 V applied DC potential in 0.5 M H_2SO_4 electrolyte. Similarly from the Fig. 1d, it could be observed that as far as the anodization is concerned, the influence of inter electrode gap is identified to be less significant.

The anodized samples have been etched in etchant solution at 298 K for different time intervals viz., 30 and 60 min respectively. The Tafel polarization results of the samples are presented in Fig. 2a and the resultant Icorr values of the samples etched for 30 and 60 min are 2.844 and 3.058 mA/cm^2 respectively. The Icorrvalue of sample after 30 minutes etching is observedto experience a quantum jump when compared to un-etched anodized sample. Furthermore increase in etching time has not observed to yield remarkable increase in Icorr values. This result infers that, the etching of anodized sample for 30 min is sufficient to remove superficial Al_2O_3 layer. Hence the anodized samples after 30 min etching have been subjected to anodization once again in order to create porous Al_2O_3 layer and this process is usually referred to as double anodization in literatures.



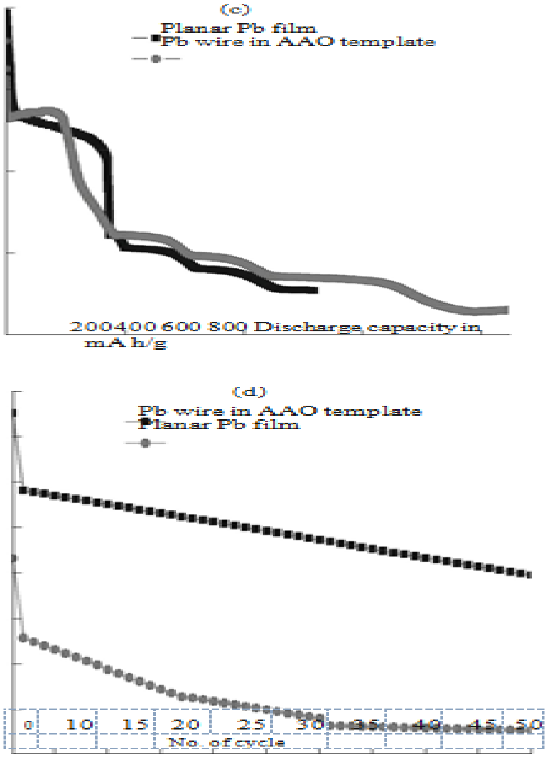


Fig. 3. (a) Scanning electron micrograph of AAO template. (b) Scanning electron micrograph of Pb nano wires. (c) Dischargeperformance of planar Pb and Pb nano wire. (d) Cycle life analysis of planar Pb and Pb nano wire.

3.2. Structural Analysis of Films

The X-ray diffraction results of aluminium thin films deposited over copper substrate at 298 and 573 K are presented in Fig. 2b. From Fig. 2b, it may be inferred that crystalline aluminium formation occurs while deposition at high temperature (i.e 573 K). Hence for further anodization, the aluminium thin films deposited at 573 K have been preferred. From the Figure 2b it could also be observed that the diffractogram of A3 sample corresponding to anodization in 0.5 M H_2SO_4 by applying 20 V does not possess any characteristic peak of Al_2O_3. This effect may be attributed to the amorphous nature of the Al2O3 layer and the inference coincides with the observations of other researchers [9]. Nevertheless, a broader hump centered around two theta 35 degrees is observed in the Fig. 2c for the A3 sample, which is considered to be figure print of amorphous γ-Al2O3 layer [10]. Moreover, it is also observed that the intensity of the peak corresponding to aluminium decreases with the advent of anodization.

In Figs. 2b and 2c, the diffractogram of A4 corresponding to sample that is anodized and subsequently etched for 30 min has not shown the presence of Al2O3 layer. Moreover, the intensity of peaks corresponding to aluminium are observed to sharply increase upon etching, which may be corroborated to complete removal of superficial Al2O3 layer resting over alumin-ium thin film. The diffractogram of sample A5 sub-jected to double anodization for 30 min is shown in Fig. 2b and from which it may be observed that the (220)peak corresponding to aluminium fades with double anodization. This fading may be corroborated to the adherent porous Al2O3 layer formation over the substrate.

3.3. Morphological Analysis

The SEM micrographs of the doubly anodized porous sample and Co electrodeposited anodized samples are presented in Figs. 3a and 3b respectively. The micrographs have been subjected to Image processing analysis using Image-J software and the poros-ity, mean pore aspect ratio of anodized porous tem-plate are calculated to be 38.8% and 1.509 respectively. From the micrographs the uniformly distributed pores throughout the anodized sample surface is evident and similarly the growth of Co metallic wires from the pores is also evident. The aspect ratio of Pb wire grown over AAO template is calculated to be around 1.668 and the mean diameter of wire is calculated to be around 75 nm and the thickness of porous alumina layer superficially formed over the aluminium is calculated using 3D image processing of SEM micrograph and it is observed to be around 45 nm.

3.4. Battery Testing

The discharge profiles of the Pb wire anode in AAO template and Pb thinfilm electro deposited on copper substrate are presented in Fig. 3c. From the Fig. 3c it may be observed that Pb wire anode has better discharge capacity when compared to planar Pb film. Moreover, the extent of Li alloying is higher in Pb wire and sequential Li–Pb alloy phase occurring in each voltage plateau shown in the Fig. 3c illustrates maxi-mum Li–Pb alloying occurring in wire anode. The cyclability of the batteries with Pb wire and planar anodes are presented in Fig. 3d and from which, both the anodes are observed to possess loss in Coulombic efficiency between first cycle and second cycle. The capacity retention after second cycle of Pb wire anode and of planar Pbfilm anode is 80 and 67% respectively. After second cycle, both the anodes have shown stable decrement in capacity and the percentage capacity retention after 50th cycle on comparison with second cycle of Pb wire anode and Pb planar film anode is 72.6 and 43% respectively.

4. CONCLUSIONS

The process of creating anodic alumina template over sputtered aluminium thin film through double step electrochemical oxidation in H2SO4 medium has been exemplified. The comprehensive investigation of anodization through Tafel polarization has illustrated better results in 0.5 M H2SO4 while applying 20 V DC potential for 30 minutes. The SEM analysis have shown uniformly distributed pore with size around 0.075 µm and pore aspect ratio around 1.509. The Co wires grown projected from the surface observed from SEM analysis possess mean diameter of 75 nm. The Co wires grown over AAO template have shown 1.6 times higher specific discharge capacity when compared to Pb planar film anode. The capacity retention of Pb wire anode is also 1.55 times greater than Pb planar anode. Hence it may be concluded that the Pb wire anode may be a futuristic candidate for improving the energy density of existing Li ion battery systems.

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