



## Electrochemical Activities of Melamine and its Applications in Aqueous Rechargeable Lithium Ion Batteries

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### ABSTRACT

The organic molecules with electroactive centers play a very important role in the field of aqueous and non-aqueous rechargeable lithium ion batteries. A triazine derivative called melamine with three amine groups provide the seat for lithiation/delithiation during charge discharge process. In this work, we proposed a suitable and stable novel electrode material for aqueous rechargeable lithium-ion battery with an excellent average cell voltage of 1.19 V with cyclizability and a good discharge capacity of about 90 mAh g<sup>-1</sup> in an aqueous electrolyte. The electrochemical performances were performed under the ambient temperature and pH to obtain characteristic kinetics of electrode reaction. Preferential electrochemical methods for the study of battery applications have been done by means of cyclic voltammetry, galvanostatic cycling with potential limitation battery testing procedure, and the kinetic parameters were stipulated by electrochemical impedance spectroscopy methods.

**Key words:** Aqueous rechargeable lithium-ion battery, Melamine, Cyclic voltammetry, Galvanostatic cycling with potential limit, Electrochemical impedance spectroscopy.

### 1. INTRODUCTION

The applications of lithium-ion batteries have been extended to a wide range from portable electronics to electrical vehicles [1]. In order to fulfill these applications, the utilization of higher capacity electrode materials in energy storage devices had been a keen interest of researcher. In this regard, researchers put forwarded their efforts in the development of electrode materials by using available resources to reach the actual needs [2]. The early developments in this were field focused on the inorganic resources for electrode materials, which facilitated with the requirements for better output [1]. Such innovative strategy in the field of energy storage technology is shifting from traditional inorganic compounds to new organic alternatives in order to obtain the good results. The usage of such low cost, eco-friendly electroactive species such as organic molecules is one of the criteria to develop them as electrode material [1,2]. Nevertheless, the active centers in the electrode species such as carbonyl, hydroxyl, conjugated systems, organosulfur compounds, quinones, carboxyl groups, trioxotriangulene, [3] etc., play a major role in the insertion of Lithium ion during electrochemical performance.

In the present work, we reported that the electrochemical activities of an organic species with multiple active centers with caged structure called melamine (MEL) in an aqueous media. The studies such as cyclic voltammetric, battery testing process, and kinetics of lithiated MEL were carried out under constant pH and temperature. The experimental results of this organic species have confirmed an improved performance at boundary conditions, which facilitates the utilization of MEL in energy sources in future day.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials and Reagents

Chemicals and reagents, which were used for our experiments, such as MEL, LiOH, polytetrafluoroethylene powder (12 μ), N-methyl-2-pyrrolidone, and lithium sulfate were procured from Sigma Aldrich. The physical characterization of the Li-MEL was done by powder X-ray diffraction (pXRD) using AXRD Bench-top powder diffraction system and scanning electron microscope (SEM) by using TESCAN GAIA3.

#### 2.2. Lithiation of MEL

For the application of MEL in the field of lithium ion battery, the lithiation of starting material was carried

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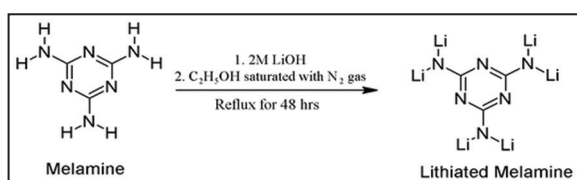
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out under an inert atmosphere. The 1 mole solution of lithium hydroxide in oxygen free water was added drop-wise to a solution of MEL in oxygen free alcohol. The mixture was stirred at 80°C for 48 h [4]. The possible lithiation of MEL is predicted in Scheme 1.

### 2.3. Electrochemical Analysis

The electrochemical studies were carried out in an aqueous medium by using 2 M lithium sulfate solution. A stoichiometric ratio of Li-MEL, carbon black, and binder polytetrafluoroacetylene was mixed and made in slurry with few drops of N-methyl-2-pyrrolidone [5], the slurry was coated on stain steel mesh electrode and dried at 100°C for 10 h under vacuum. For the cyclic voltammetry (CV) and impedance measurements, a standard three-electrode system was enabled.



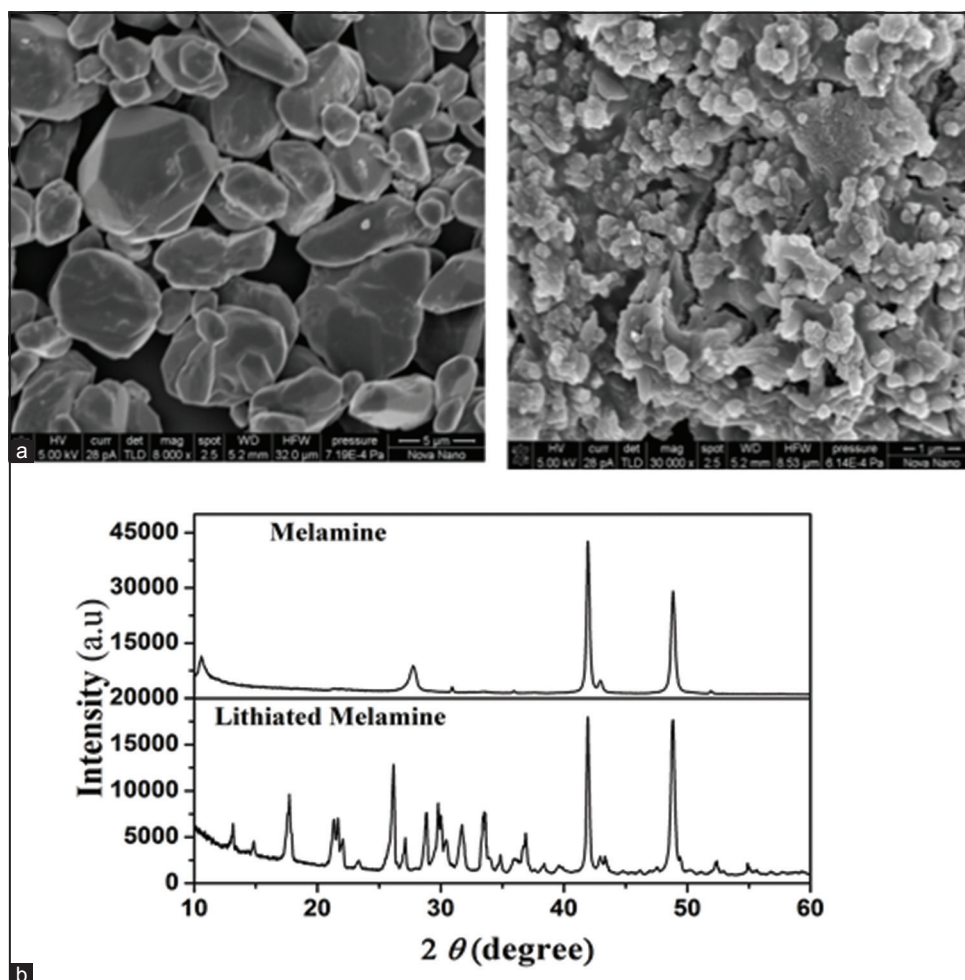
**Scheme 1:** Synthesis of Li-MEL from MEL.

A saturated calomel electrode and a platinum foil were used as reference and counter electrodes, respectively. The charge/discharge studies were performed by coupling with  $\text{LiAl}_{0.5}\text{Mn}_{0.95}\text{O}_2$  (LAM) as cathode. The potentials of electrode were cycled between  $-1.0$  V and  $0.8$  V with the scan rate of  $0.1$ - $1.0$  mV/s for CV measurements.

## 3. RESULTS AND DISCUSSION

### 3.1. Morphological and Structural Investigations

Figure 1a shows typical SEM photographs of MEL and Li-MEL, respectively. In which, a heterogeneous irregular sized granular crystal with particle size ranging from  $5$  to  $20$   $\mu\text{m}$  was obtained for MEL. From the SEM image of LiMEL, it is clear that the formation of the globules with reduced particle size to  $1$ - $5$   $\mu\text{m}$  was may be due to the lithiation. The reduced particle size facilitates the diffusion process of the electrode reaction. The pXRD patterns of both MEL and Li-MEL are shown in the Figure 1b. The XRD pattern is due to crystalline nature of MEL. Whereas in case of Li-MEL, the XRD profile, the additional peaks with broaden and lower intensity peaks corresponds to the amorphous nature [6] of the material may be due to the lithiation.



**Figure 1:** (a) scanning electron microscope photography and (b) powder X-ray diffraction profile of melamine (MEL) and Li-MEL.

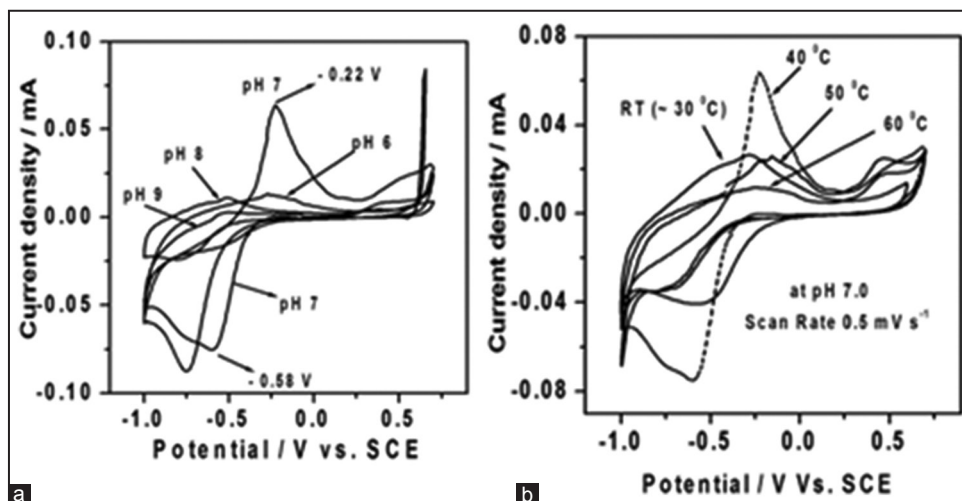


Figure 2: Cyclic Voltammogram (a) at different pH and (b) at different temperature.

### 3.2. Cyclic Voltammetric Measurements

The electrochemical investigation of Li-MEL was carried out by CV method under an applied potential  $0.5 \text{ mV s}^{-1}$  at different experimental conditions such as pH and temperature as shown in the Figure 2. During potential scanning from zero to negative sweep potential at pH 7 and 9, prominent reduction peaks were observed at  $-0.58 \text{ V}$  and  $-0.74 \text{ V}$ , respectively. These peaks were corresponding to reduction of Li-MEL. From the Figure 2a, only in neutral pH a prominent oxidation peak appeared at  $-0.22 \text{ V}$  indicates that the neutral electrolytic medium favored for Li-MEL activity. The Figure 2b was taken at  $40^\circ\text{C}$ ,  $50^\circ\text{C}$ , and  $60^\circ\text{C}$  temperature, in which the peaks with increase in peak currents at  $40^\circ\text{C}$  at similar potential as in case of pH profile, favors redox reaction of the electrode material.

### 3.3. Galvanostatic Cycling with Potential Limit

In order to determine the cell voltage, capacity, and cycling capability of Li-MEL|2M  $\text{Li}_2\text{SO}_4$ |LAM cell, the galvanostatic cycling with potential limitation studies were carried out at  $40^\circ\text{C}$  and in 7.0 pH electrolyte. An AC current of  $0.06 \text{ mA}$  was applied at C/8 rate in the potential window of  $-1.0 \text{ V}$  to  $1.3 \text{ V}$ , which delivered a discharge capacity of  $90 \text{ mAh g}^{-1}$  with an average voltage of  $1.19 \text{ V}$ . The cell capacity was calculated including the weights of both anode and cathode material, with respect to their n/p ratio 1:082 as shown in Figure 3. As per literature, the change in the pH and temperature of the electrolyte directly affects the cycling performance of the cell and capacity loss [7].

### 3.4. Potentiostatic Electrochemical Impedance Spectroscopy

Figure 4 shows the complex impedance spectrum (Nyquist Plot) of Li-MEL measured at different potential. From the Figure 4, it is clear that the appearance of semicircles at potential scan before and after insertion and deinsertion process due to the

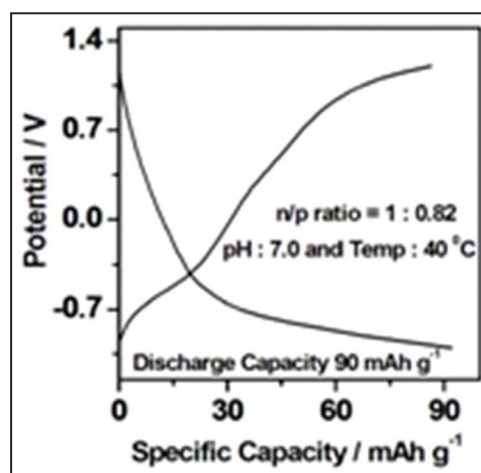


Figure 3: The GCPL profile of Li-melamine|2M  $\text{Li}_2\text{SO}_4$ |LAM cell.

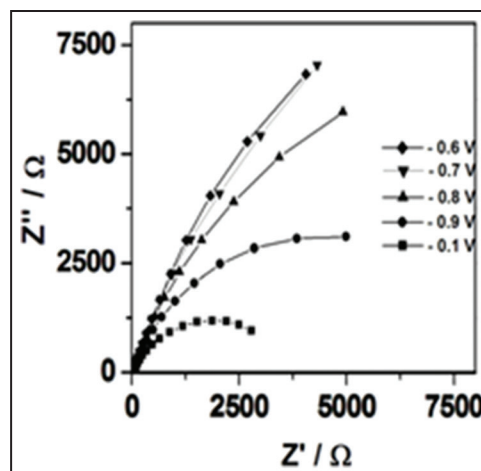


Figure 4: Nyquist plots to show the impedance measurements at different potential bias.

bulk conductivity of the lithium ions in electrolyte electrode interface. Herewith, the impedance spectra corresponding at peak potential with prominent

Warburg impedance at low frequency region may be attributed to the limitations of mass transfer from bulk to the outer surface of the electrode [8].

#### 4. CONCLUSION

The detailed electrochemical investigation reveals that, the electrochemical performance of lithiated MEL favored at neutral pH at 40°C. The average cell voltage of 1.19 V with an appreciable capacity around 90 mA h g<sup>-1</sup> is an impressive coverage of MEL analog. The significant characteristic of lithiated MEL is the appearance of Warburg lines even at very low frequencies may be because of very short voltage excitation process. These parameters have provided an ambient criterion to lithiated MEL to act as an anode material for future applications in ARLIB.

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