# Application of a Zr-Metal Organic Framework in NCPE for Lithium Battery

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## Abstract

In this study, a zirconium based Metal Organic Framework (MOF) is synthesized and is used as a nano-filler for a polymeric matrix in Li-ion battery electrolyte. Nanopoweder of Zr-BTC was prepared using solvothermal method and Initial electrolyte, consisting of polymethylmethaacrylate (PMMA) and LiTFSI, was prepared via cast solution technique. To identify MOF, many methods including PXRD, SEM, thermogravimetric analysis (TGA), FT-IR and charge/discharge tests were applied.

## Introduction

In recent decades, development of Li-Battery technology is due to the transition from traditional liquid electrolytes to solid state electrolytes [1]. The metal-organic frameworks are widely used in batteries attribute to their huge surface area, high porosity, low density, controllable structure and tunable pore size that can favor the electrochemical reaction, interfacial charge transport, and provide short diffusion paths for ions [2]. MOFs having porous structure, exhibit high surface area which gives them a variety of applications in storage of gases, catalysis, adsorption and removal of heavy metals and dyes, drug delivery and etc. These days, MOFs are extensively used in batteries and super-capacitors [3].

A Nano-composite polymer electrolyte (NCPE) is prepared via cast-solution method by which Zr-BTC MOF, benzene-1,3,5-tricarboxylic acid (H3BTC), and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) are used as fillers for poly methyl metacrylate (PMMA) matrices. These polymer electrolytes react well in electrochemical reactions and MOF will increase the ionic conductivity of the nano-composite electrolyte therefore the charge/discharge efficiency will be enhanced [4].

## Material and method

All chemicals, including $ZrCl_4$ and $H_3BTC$ (Benzene-1, 3, 5-tricarboxylic acid, 98.9%) was supplied by Sigma–Aldrich. DMF (Dimethylformamide 99%) and chloroform (99%) and dimethyl acetamide by Merck, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and poly methyl metacrylate (PMMA) were supplied by Sigma–Aldrich. All chemicals were of high purity and used without any further treatment.

## Preparation of Zr-BTC MOF

Zr-MOF was synthesized by scaling-up a previous procedure, with some changes. Typically, $ZrCl_4$ and BTC and 1 ml acetic acid were mixed in DMF and dispersed with the assistance of ultrasonication, then placed in an autoclave. A resulting white product was filtered off, washed with DMF, and immersed in a chloroform solution. After separation by filtration, the solid sample was dried under vacuum. Crystallization was carried out under static conditions. The activation using chloroform is efficient to remove molecules of DMF and unreacted BTC from the pores enhancing porous structure and surface area [5].

## Preparation of nano-composite polymer electrolyte by casting method

In this method, a solution of salt in dimethyl acetamide was prepared to build molarity specified. The solution stirred at 50° C for 5 hours to a homogeneous solution. The nano-filler was added to the polymer under sonication until a homogeneous solution obtained. Then heating for 20 hours removed the solvent. Finally, a 100-150 micrometer-thick polymeric electrolyte was obtained.

## Results and discussion

XRD pattern of Zr-MOF

Fig.1 shows the XRD pattern of simulated sample and synthesized sample by solvothermal method. The formation of our structure is confirmed by comparing with the synthesized sample (Fig. 1) and also with theoretical powder pattern [5].

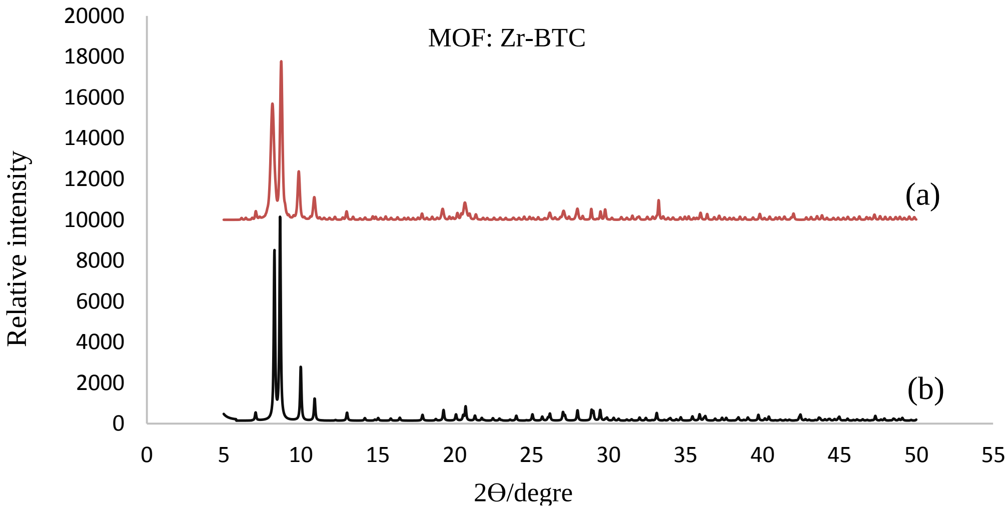

Fig.1. XRD pathern of the Zr-BTC (a) experimental (b) simulated.

## SEM analysis of Zr-MOF

The sample has shown a morphology consisting of irregular intergrown microcrystalline polyhedra, as in Fig. 2. It can be seen that crystallite size of Zr-MOF was similar to cubic shape with about 200-500 nm size.

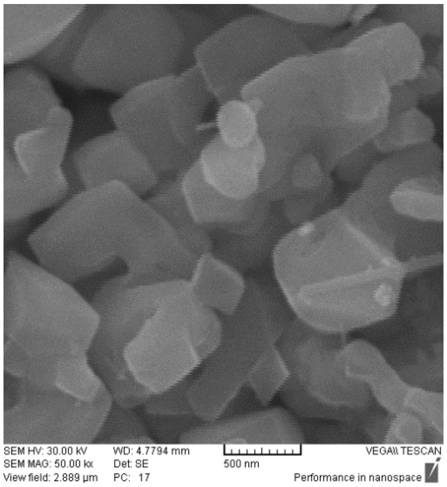

Fig.2. SEM images of the Zr-BTC MOF

## FTIR spectrum of Zr-MOF

In Fig. 3. Observed data from the FTIR of synthesized sample is similar to previous result in other papers [5].

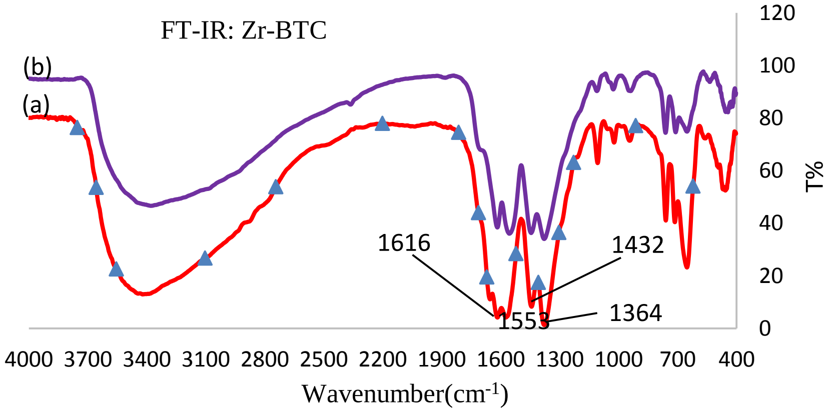

Fig. 3. FTIR spectra of Zr-BTC (a) experimental (b) simulated

TGA

Fig. 4 illustrates the TGA related to Zr-BTC, which exhibits two stages in weight loss. The first stage can be attributed to the surface water and solvent evaporation at 50-150 °C. The compound was stable at 170-520 °C and in the second stage, 530-680 °C the organic materials were decomposed and omitted [5].

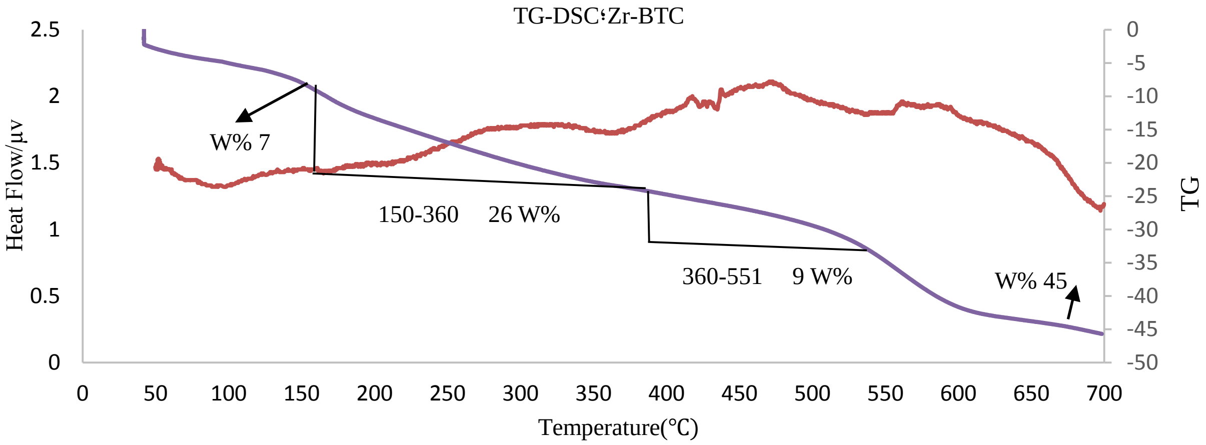

Fig.4. TGA analysis for the MOF: Zr-BTC

## The results of charge/discharge

After reviewing the results of charging and discharging, the polymer electrolyte without and with MOF as filler has almost the same capacity For this purpose, the nanocomposite polymer electrolyte with filler was used.

Charge tests were performed using a CC–CV charge, which means charging continued at 4.3V in 1C until the current reached a value corresponding to 0.03C, and then discharged to 2.8V cut-off potential in constant current 1C [6,7]. The initial charge-discharge curves of all samples at 0.1C (1C = 160 mA $g^{-1}$) between 2.8 and 4.3 V vs. $Li^+$/Li at room temperature have been performed.

The curve of the sample with the filler, is shown in Fig. 5.

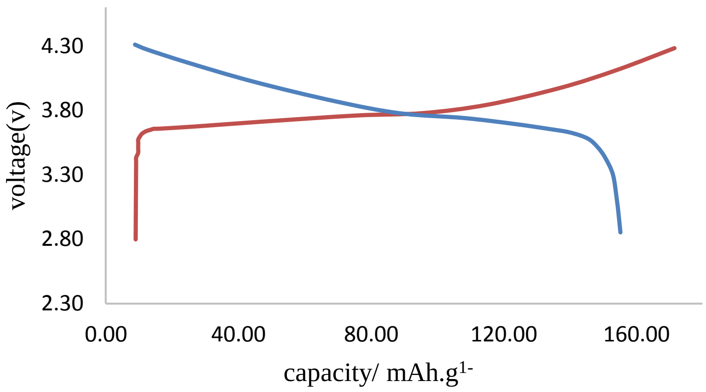

Fig.5. Initial charge–discharge curves of NCPE- MOF

## Conclusions

A nano Porous Zr-MOF with high thermal stability was synthesized by a modified procedure after effective activation processes using solvent exchange method. The activation using chloroform is efficient to remove molecules of DMF and unreacted BTC from the pores enhancing porous structure and surface area and smaller grain size. Then the MOF synthesis was used as filler in polymer electrolyte. By adding the optimum percentage of MOF effective results in charge/discharge (1C = 160 mA $g^{-1}$) was obtained.

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