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Utilization of MOF Materials for Enhanced Performance in Electrochemical Energy Devices

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Background

The demand of energy has gradually increased and it has become a threat for the future generation. The depletion of fossil fuel based economy has raised the interest in the field of electrochemical energy storage and conversion devices. Batteries and fuel-cells are some of the most important energy storage devices for the social development. Despite of having many electrochemical energy storage devices, its commercialization has been hindered due to several factors associated with its performance. Therefore there is an urge to overcome these performance and cost related limitations to fulfil the future energy demand. Metal–organic frameworks (MOFs), a novel type of porous crystalline materials, have attracted increasing attention in clean energy applications due to their high surface area, permanent porosity, and controllable structures. Unceasing research on the exploration of MOF utilization in energy applications has inspired us to work in this fascinating field. Considering the vitality of these energy devices, the present research work will be addressing various hurdle stones in each of this technologies and a possible solution to overcome these problems.

Aim

The present work aims to utilize MOF in three different fields discussed below:

1. Li-ion batteries- Ionic liquid incorporated modified MOFs as a better and safer electrolyte system for Li-ion batteries.
2. Zinc-air batteries- Surface modification of zinc anodes with MOF and polythiophene to reduce self -corrosion and improve discharge performance.
3. ORR electrocatalysts- MOFs with active carbon material will be tested for its efficiency as electrocatalysts for ORR in fuel cells and metal-air batteries.

Results and Discussion

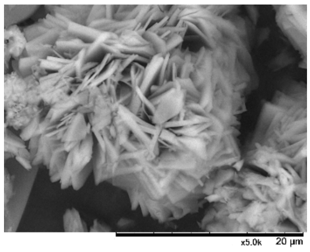

Fig. 1 SEM image of MOF (IL).

In the Chapter 2, an ionic liquid incorporated modified MOF was synthesized to serve as an efficient electrolyte system for Li-ion batteries (**Fig. 1**). Further, the MOF (IL) was doped with a lithium salt, lithium bis(triflouromethylsulfonyl) imide (LiTFSI) by a modified procedure. Samples with varying amount of MOF (IL) in ionic liquid were prepared, characterized and evaluated for their electrochemical behavior. Three samples with different weight % of MOF-5(IL) in AMImTFSI were prepared and ionic conductivity measurements were performed by AC impedance method. A high conductivity in order of 10^{-2}-10^{-3} Scm^{-1} at 51°C and a low activation energy of ion transport was observed in all samples (Table 1). The systems showed high electrochemical stability to be employed as gel electrolyte in Li ion secondary batteries. These systems showed highly reversible capacity of over 3000 $mAhg^{-1}$ in the charge-discharge studies carried out after fabricating anodic half-cell composed of Si/electrolyte/Li as shown in **Fig. 2.** These results illustrated the feasibility of the prepared modified MOF (IL) as potential solid state electrolytes for Li ion secondary batteries.

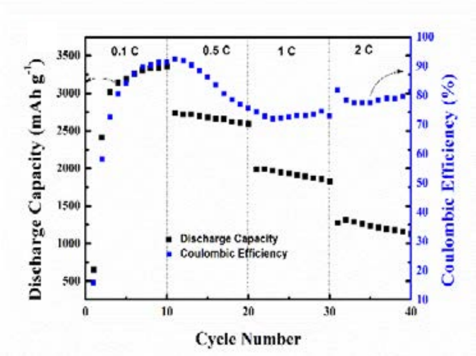

Fig. 2 Rate cycling performance of Li/electrolyte/Si cell fabricated using **30 wt%** MOF (IL) in AMImTFSI with 30 µL of EC : DEC = 1:1 for 40 cycles.

Table 1: VFT parameters for different compositions of MOF (IL) in AMImTFSI

Sample in AMImTFSI	**A($Scm^{-1}K^{1/2}$)**	**B(K)**	**R^2**	**σ (324K) Scm^{-1}**
10 wt%	11.21	722.4	0.999	1.0×10^{-2}
20 wt%	3.99	662.2	0.998	5.0×10^{-3}
30 wt%	1.88	636.5	0.998	2.3×10^{-3}

In the Chapter 3, for the first time use of MOFs for surface modification of zinc anode has been explored. In this research the use of electrochemically modified Zn electrode decorated with MOF-5 (IL) for the fabrication of Zn-air batteries is focussed upon. The research also deals with the use of polythiophene (PTh) in Zn-air batteries.

Modified MOF-5 (IL) was successfully synthesized over the zinc electrode by a mild in-situ electrochemical method using 1-butyl-3-methylimidazolium chloride (BMImCl) ionic liquid as a templating agent (**Fig. 3**). After the synthesis of MOF-5 (IL), controlled electro-polymerization of thiophene was also done over the Zn electrodes. The as-synthesized MOF-5 (IL) and PTh@ MOF-5 (IL) were characterized by using XRD and SEM. The corrosion behavior of Zn anode with different surface modifications was investigated by employing potentio-dynamic experiment in a conventional 3-electrode setup. Chronopotentiometry experiment was performed to see the discharge behavior of different Zn based anodes. The zinc air battery with pure zinc as anode showed current density of ~ 7 mA cm^{-2}. On the contrary, zinc air batteries with zinc

Fig. 3 Illustration of growth of MOF-5 (IL) films on zinc surface during electrochemical synthesis.

anodes decorated with MOF-5 (IL) showed 4 times enhanced current density of ~ 27-30 mA cm^{-2} as shown in **Fig. 4**. Considering corrosion current and current density, MOF (IL) decorated Zn anodes and PTh@ MOF (IL) coated Zn anodes showed the most favourable characteristics to be used in zinc-air batteries. In conclusion, the modified Zn electrodes with MOF can be prospective anodes in Zn-air batteries.

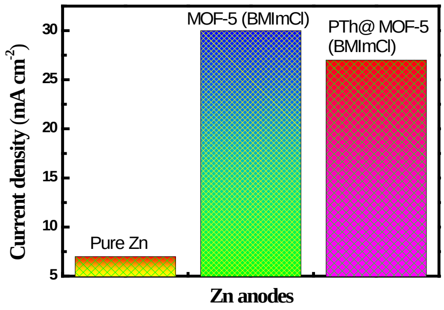

Fig. 4 Comparison of current densities of cells fabricated using pure Zn and modified Zn anodes.

In Chapter 4, novel hybrid nano composites of ZIF-8 and FAB were synthesized which integrates the unique properties of two fascinating materials to design efficient non precious metal catalysts for ORR. For the synthesis of ZIF-8/FAB nano composites, X wt% (X=2, 5, 10) of FAB-methanol solution was added during the preparation of ZIF-8 nano crystals in the strring condition. The resultant solution was centrifuged and washed several times with water-methanol mixture and dried at 80 ^oC to obtain ZIF-8/FAB nano composites. XRD, IR and TEM (**Fig. 5(a)**) were employed to characterize the material successfully. The ORR performance of the hybrid nano composite was evaluated using cyclic voltammetry. Cylic voltammetry curves (**Fig. 5(b)**) revealed clear oxygen reduction peak for the synthesized ZIF-8/FAB nano composite in O_2 saturated 0.1 M KOH solution comparing with that in N_2 saturated solution, implying an oxygen reduction activity.

In conclusion, a simple procedure to prepare hybrid ZIF-8/FAB nano composite was demonstrated which shows excellent activity towards oxygen reduction. To the best of my knowledge, this is the first account of the growth and stabilization of ZIF-8 nanocrystals over FAB with high electrocatalytic activity and methanol tolerance.

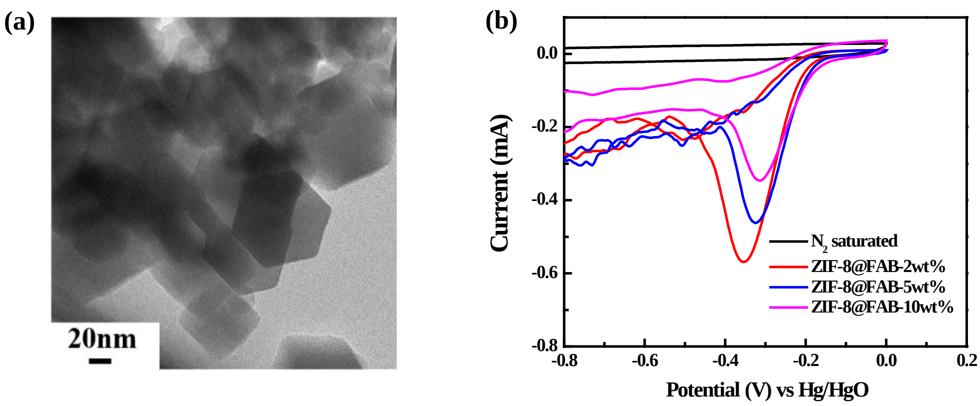

Fig: 5 (a) TEM image of ZIF-8/FAB-2 wt%, **(b)** CVs of ZIF-8@FAB-2wt%, ZIF-8@FAB-5wt% and ZIF-8@FAB-10wt% nanocomposites in N_2-or O_2 saturated 0.1M KOH solution.

Keywords: Metal Organic Frameworks (MOFs), Ionic Liquids (ILs), Li-ion Batteries Electrolytes, Zinc-air batteries, Electrochemical Synthesis, Oxygen Reduction Reaction (ORR)

Table of Contents:

A) Publication (Peer Reviewed):

1) **Ankit Singh**, Raman Vedarajan and Noriyoshi Matsumi, “Modified Metal Organic Frameworks (MOFs)/Ionic Liquid Matrices for Efficient Charge Storage”, **J. Electrochem. Soc., 2017, 164 (8), H5169-H5174.**

B) Manuscript (In preparation):

1) **Ankit Singh**, Raman Vedarajan and Noriyoshi Matsumi, “Surface Modification of Zn Anode by MOFs Coating for Improved Zn-Air Batteries”. **(In editing phase)**
2) **Ankit Singh**, Raman Vedarajan and Noriyoshi Matsumi, “ZIF-8/Functionalised Acetylene Black (FAB) Hybrid Nanocomposites As Efficient Non Precious Metal Catalyst For ORR”. **(In editing phase)**