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論　　文　　題　　目	Utilization of MOF Materials for Enhanced Performance in Electrochemical Energy Devices
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論文の内容の要旨

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

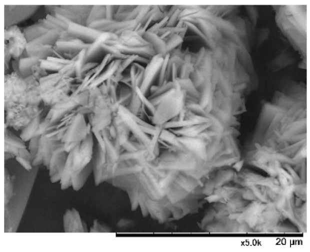

Fig. 1 SEM image of MOF

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

Sample in AMImTFSI	**A($Scm^{-1}K^{1/2}$)**	**B(K)**	**R^2**	**σ (324K) Scm^{-1}**

MOF (IL) as potential solid state electrolytes for Li ion secondary batteries.

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}

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

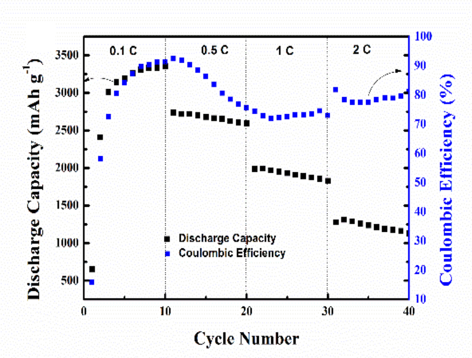

Fig. 2 Rate cycling performance of Li/electrolyte/Si cell fabricated using **30 wt%** MOF (IL) in AMImTFSI with 30 µL

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.

Fig. 3 Illustration of growth of MOF-5 (IL) films

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 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.

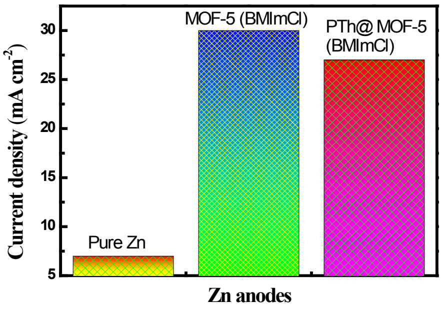

Fig. 4 Comparison of current densities of cells fabricated using pure Zn and modified Zn anodes.

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 ^{o}C 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.

(a)

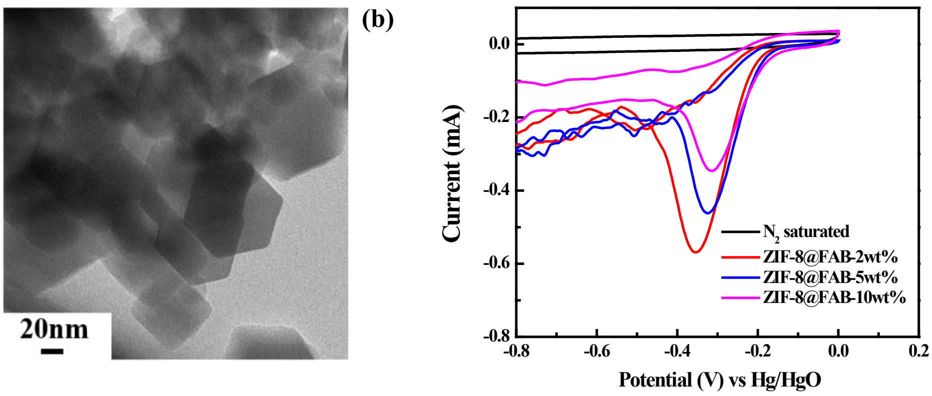

Fig: 5 (a) TEM image of ZIF-8/FAB-2 wt%, **(b)** *CVs of ZIF-8@FAB-2wt%, ZIF-8@FAB-5wt% and ZIF-8@FAB-10wt% nanocomposites in N_2-or O_2 saturated 0.1M KOH solution.*

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

論文審査の結果の要旨

本論文は MOF (Metal-Organic-Framework)系材料をリチウムイオン２次電池用電解質、亜鉛—空気電池用電極被膜材料、燃料電池用酸素還元反応触媒としてそれぞれ活用することを検討したものである。

リチウムイオン２次電池における MOF 系材料の活用例としては、電極材料の表面積を高める目的で活用されていた事例が多く、電解質としての応用は極めて限られていた。電解質のリチウムイオン伝導性を高めるためのアプローチとしては、電解質のイオン輸送チャンネルに構造的秩序を導入することによりイオン輸送の活性化エネルギーを低下させることが有効と考えられており、液晶構造の導入などが検討されてきた。本研究ではイオン液体をテンプレートとして電気化学的に MOF を形成させる反応を活用しつつ、得られた MOF 系材料の内部にリチウム塩を導入することにより、擬固体型イオン液体/MOF マトリックスのイオン輸送活性化エネルギーを大幅に低減させつつ 10^{-3} Scm^{-1} 以上のイオン伝導度を観測した。本系は 5.2 V 以上（vs Li/Li^{+}）

の電位窓を示し、高電圧型の電極系にも対応しうる電気化学的安定性を有することが分かった。さらに、Li/電解質/Si 型ハーフセルを構築して充放電測定を行ったところ 3000 mAg^{-1} 以上の放電容量が達成された。

また、リチウムイオン２次電池の４倍程度の理論エネルギー密度を有することが知られている亜鉛—空気電池において、亜鉛板上への電気化学的 MOF 形成を活用した耐腐食コーティングの効果を検討した。亜鉛—空気電池においては電気化学的水分解などの副反応に伴い電極表面に水酸化亜鉛が形成され、放電に伴ってパフォーマンスが急速に低下する挙動が知られている。亜鉛と電解液の直接的な接触をコントロールしつつイオンの溶出と浸透を許容する被膜を開発することにより電池系の持続性を向上させることが望まれている。本研究では電気化学的 MOF コーティングと電解重合によるポリチオフェン修飾を組み合わせることにより放電時の電流密度を４倍まで高めることに成功した。

さらに、剥離アセチレンブラック上に ZIF (Zeolitic Imidazolate Framework)-8 を結晶生成させることにより、非貴金属型の優れた酸素還元反応触媒を設計した。酸素還元反応に伴う電流は酸素雰囲気下においてのみ観測され、メタノール存在下においても活性は低下しなかった。特筆すべきもう一つの点は、本材料の作製においてアニーリング処理は一切行っておらず、低温で材料合成が可能なことである。本手法は官能基密度が高い剥離アセチレンブラックを用いることで有効に機能していると考えられ、構造の明確な材料から成る高電気化学触媒活性コンポジットのデザインに有効と期待される。

以上のことから本論文は学術的な新規性と有用性を有する多くの知見を示していることから、博士（マテリアルサイエンス）の学位に値するものと認めた。