

Title	ビスイミノアセナフテン構造を有する材料の合成と電気化学エネルギーデバイスへの応用
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Synthesis of Bisiminoacenaphthene (BIAN) Based Materials and Their Application to Electrochemical Energy Devices

Chapter 1: Background

The current thesis is focused on compounds of the family bis(aryl)acenaphthenediimine (Ar-BIAN) (Figure 1). They have long been employed as ligands for transition metals and their metal complexes have been utilized as catalysts in wide spectrum of reactions. However only recently the rich redox chemistry of Ar-BIAN based compounds have been evaluated. These compounds are characterized by high chemical stability and have wide scope for functionalization owing to the availability of suitable precursors. And more importantly, they have the inherent ability to act as electron sponge in a reversible manner. Feudskin and coworkers have shown that these group of ligands can easily take up to four electrons from reactive metals like Na/Li and form corresponding complexes, which can also disproportionate to come back to their original state. This ability to stabilize various reactive metals in redox active manner can thus have interesting applications in energy storage devices. By utilizing these group of materials on electrode surface, their electron reservoir property can help in providing better interfacial characteristics, especially when the interface is a dynamic one. Hence, in an effort to capitalize on these unexplored but potential properties of these group of materials, we synthesis various functional materials with end applications in Li-ion and Li-air based energy devices. (Figure 2)

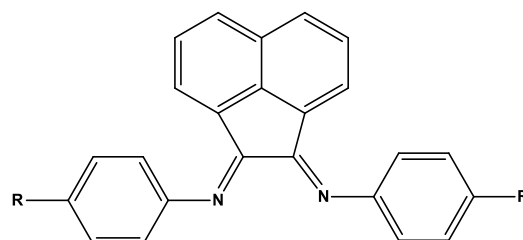


Figure 1. Bis(aryl)acenaphthenequinonediimine

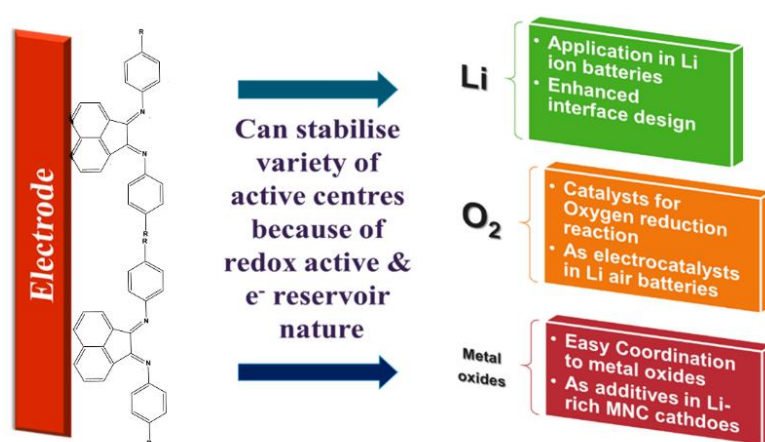


Figure 2. Graphical abstract of current research

Chapter 2: BIAN based polymer binder

First line of research was focused on designing BIAN based binder materials for Li-ion batteries (LiB's). The application of band gap engineered binders can have great effect on the ultimate device performance, even though binder constitute only a small fraction of the gravimetric weight of the electrode. Our results showed that, use of BIAN based functional diamine polymer binder leads to performance improvement resulting from an enhanced SEI.

Bis-imino-acenaphthequinone (BIAN)-Fluorene copolymer (π conjugated polymer bearing BIAN and fluorene units) binder (Figure 3) was designed, synthesised and adopted for preparation of graphite electrode laminate in lithium-ion batteries. Density functional theory calculations using Gaussian 09 showed that the polymer had Lowest unoccupied molecular orbitals (LUMO) levels lower than that of the LUMO of carbonate based electrolytes and hence would undergo reduction before the reduction of the

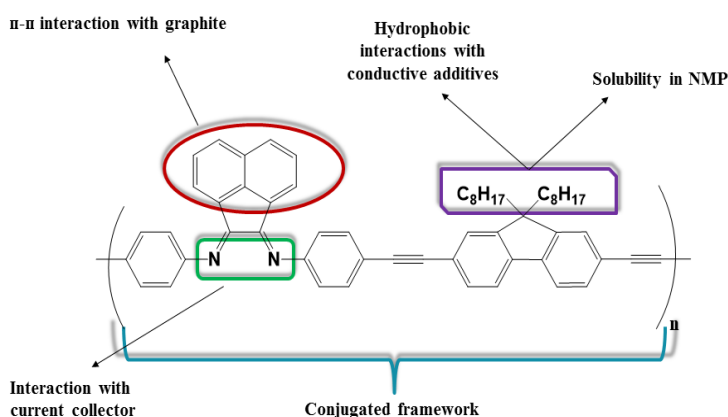


Figure 3. Functional components of BIAN-Fluorene biunder

of graphite electrode laminate in lithium-ion batteries. Density functional theory calculations using Gaussian 09 showed that the polymer had Lowest unoccupied molecular orbitals (LUMO) levels lower than that of the LUMO of carbonate based electrolytes and hence would undergo reduction before the reduction of the

electrolyte components. This in turn would reduce irreversible electrolyte reduction on binder surface (Figure 4). More importantly, the resultant SEI derived from the reduced conjugated polymer will be more robust compared to conventional electrolyte reduction derived SEI. Compared to the traditional PVDF binder, the electrode with BIAN-Fluorene binder exhibited significantly enhanced electrochemical performance in terms of rate capability, specific capacity and cycling behavior. At a rate of 1C, the electrode with BIAN-Fluorene binder exhibited more than 250 mAhg^{-1} capacity after 100 cycles while the electrode based on PVDF binder only delivered 165 mAhg^{-1} . The significant improvement of cycling performance was due to the improvement of adherence of the electrode laminate to the current collector and improved interface. Electrochemical impedance spectroscopy (EIS) and dynamic electrochemical impedance spectroscopy (DEIS) studies showed the formation of an improved interface with BIAN-Fluorene based binder.

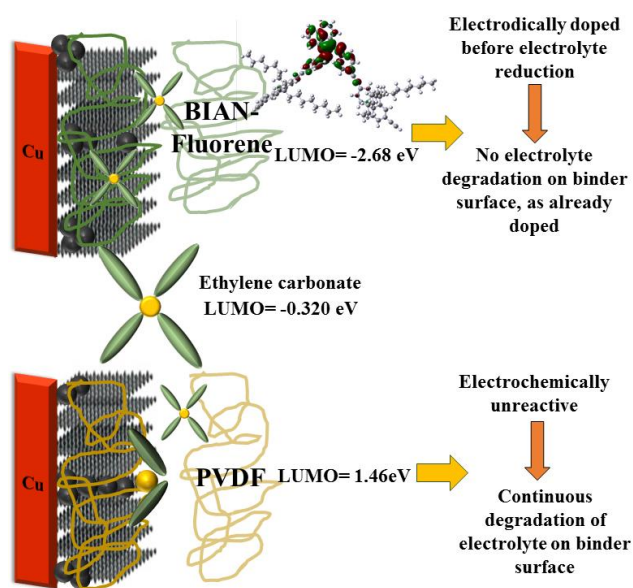


Figure 4. Graphical abstract of functioning of the novel polymer binder

Chapter 3: BIAN based polymeric electrocatalyst

The second application was to use BIAN based materials as electrocatalyst for Oxygen reduction reaction (ORR) in fuel cells and Li-air batteries. We could design active site defined polymeric electrocatalyst for ORR, for the first time. The performance of the catalyst was in par with other metal free ORR catalysts and with much higher stability than conventional Pt/Vulcan based electrocatalysts. The further development of this kind of active site defined polymeric electrocatalyst and their corresponding metal coordinated analogues will thus be a big leap in transition from random high energy consuming annealed carbon based electrocatalysts to defined materials under ambient conditions.

Design, synthesis and performance evaluation of functional polymer material with defined active sites for oxygen reduction reaction (ORR) catalytic activity in aqueous as well as non-aqueous media is reported. BIAN-paraphenylene (BP) copolymer having imine backbone (Figure 5) was synthesized via solution based polycondensation. The as synthesized polymer itself showed considerable ORR activity, comparable to that of other reported metal free heteroatom doped carbon materials. The composites of the polymer with graphene oxide (GO) sheets (GO/BP) were also synthesized under moderate temperature conditions (400°C) with the polymer remaining intact. The composites showed further enhanced electrochemical activity owing to the synergistic effect of GO and active site defined polymer material. We also tried to evaluate

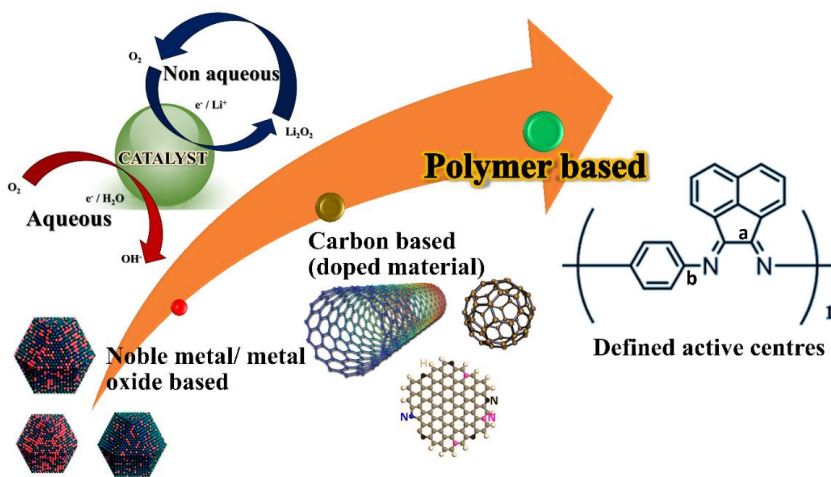


Figure 5. Schematic showing evolution of ORR catalysts and current polymeric catalyst

the nature and basis of catalytic activity on polymer surface by different techniques. The cyclic voltammograms showed two distinct ORR peaks, indicating two different active sites. This was also in agreement with Mulliken charge distribution analysis from Density functional theory (DFT) studies, which

showed the presence of two different carbons next to nitrogen having different electropositive nature. More interestingly, the polymer itself and its composites with GO showed excellent stability for ORR in non-aqueous medium and ether based solvents with dissolved lithium salts. ORR in non-aqueous solvents being the pre-requisite for utilization in Li-air batteries, the polymeric catalyst material is thus a promising alternative to conventional catalysts for ORR (Figure 6). Also, the polymer itself can be used as an ORR active binder for electrode slurry preparation, thereby enhancing catalyst performance.

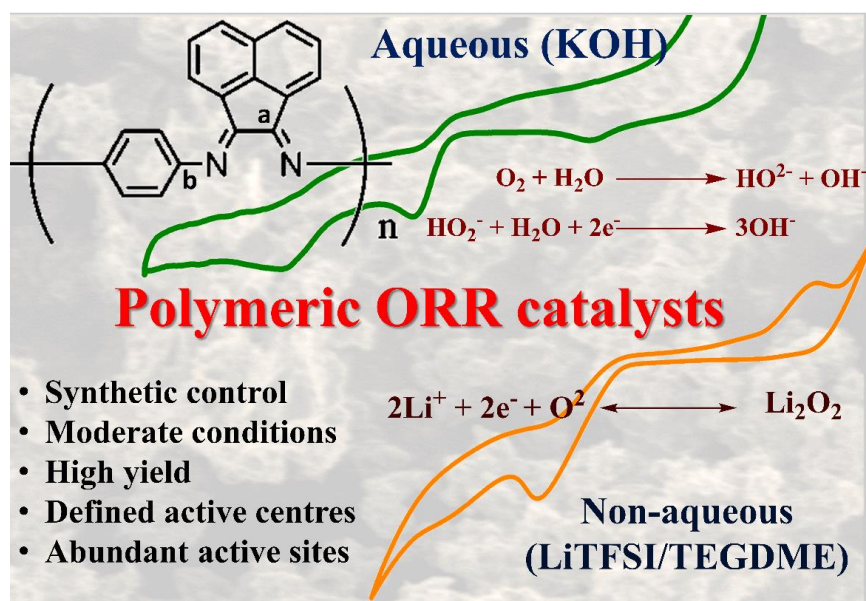


Figure 6. Graphical summary of BIAN based ORR active polymer activity

Chapter 4: BIAN based functional additive for high voltage cathodes

Inspired with these results, we further designed BIAN based band gap engineered additives for performance and storage enhancement of high voltage cathodes for LIB's (Figure 7). The results were quite promising, giving very good cycling stability and capacity retention upon storage. We also performed XPS studies to understand the surface evolution during cycling at high voltage and found that, BIAN based additive reduces irreversible electrolyte oxidation on electrode surface as compared to the case without any additives.

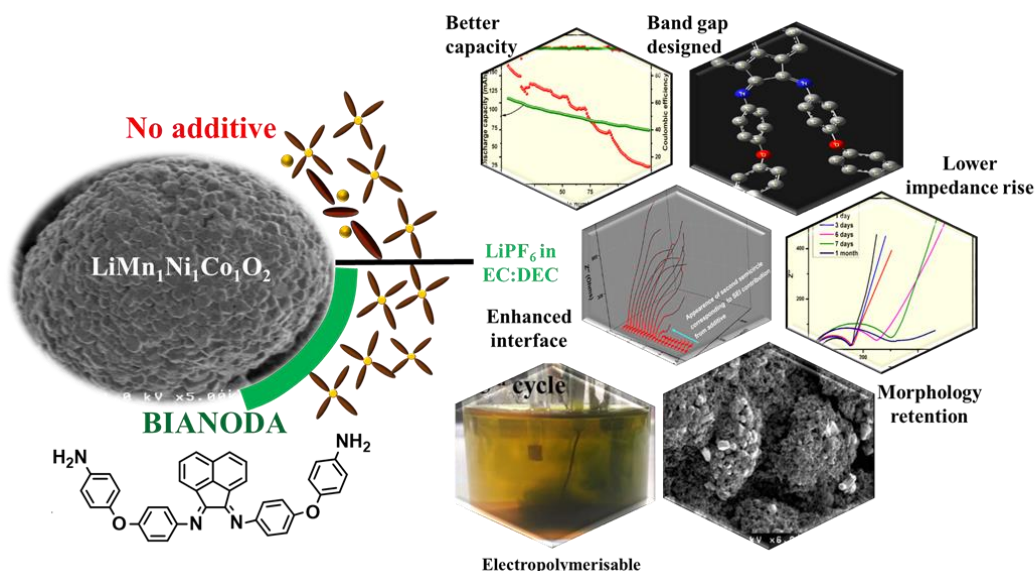


Figure 7. Graphical summary of BIANODA based functional additives for high voltage cathodes

Keywords: Bisiminoacenaphthene, binders, Li-ion batteries, oxygen reduction reaction, electrocatalysts, high voltage cathodes, electropolymerisation

