

Title	固体電解質界面(SEI)の形成制御を指向したリチウムイオン二次電池負極を高度安定化するBIAN型機能性高分子バインダーの戦略的設計
Author(s)	GUPTA, Agman
Citation	
Issue Date	2021-09
Type	Thesis or Dissertation
Text version	ETD
URL	<a href="http://hdl.handle.net/10119/17530">http://hdl.handle.net/10119/17530</a>
Rights	
Description	Supervisor:松見 紀佳, 先端科学技術研究科, 博士

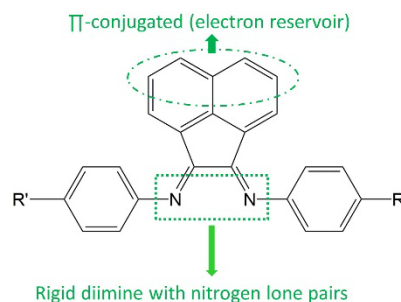
氏 名	GUPTA, Agman
学 位 の 種 類	博士（マテリアルサイエンス）
学 位 記 番 号	博材第 517 号
学 位 授 与 年 月 日	令和 3 年 9 月 24 日
論 文 題 目	Stabilizing High Performance Li Ion Battery Anodes by Strategic BIAN-based Functional Polymer Binders Design for Controlled Solid-Electrolyte Interphase Formation
論 文 審 査 委 員	松見紀佳（北陸先端科学技術大学院大学先端科学技術研究科教授） 金子達雄（北陸先端科学技術大学院大学先端科学技術研究科教授） 谷池俊明（北陸先端科学技術大学院大学先端科学技術研究科教授） 長尾祐樹（北陸先端科学技術大学院大学先端科学技術研究科准教授） 山田裕貴（大阪大学産業科学研究所教授）

## 論文の内容の要旨

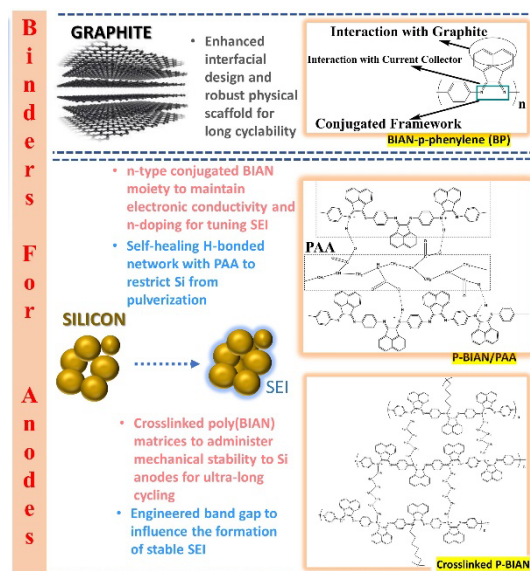
### Chapter-1: Introduction

The development of high energy density lithium-ion batteries (LIBs) for future applications in electric vehicles (EVs), hybrid electric vehicles (HEVs), portable electronic devices, etc. is one of the prime areas of research across the globe. In this regard, various suitable high-capacity alternatives like Sn, Ge, and Si have been explored to replace commercial graphite anode in a LIB. Among various alternatives, Si has been recognized as the next generation anode active material because of its high theoretical capacity ( $\sim 4200 \text{ mAhg}^{-1}$ ) and natural abundance. However, commercial graphite anode and its potential next generation alternative Si have their own sets of drawbacks. But the quality of solid-electrolyte interphase (SEI) is one common drawback associated with both that destabilizes their long-term cycling performance with poor reversible capacity. As a remedy to mitigate all the drawbacks, especially those associated with the interphase formation on these anodes, the utilization of polymers as binders has been recognized as a good strategy. Compounds of the family bis(aryl)acenaphthenequinonediimine (Ar-BIAN) are famous for their ability to act as ligand for transition metal

complexes in catalysis as they can act as electron reservoir and offer rich redox chemistry (Figure 1). Also, they have exhibited impressive synthetic versatility as they are potent with structural modification, functionalization, and have tunable electronic properties because of the availability of suitable precursors. Most importantly, their low-lying lowest unoccupied molecular orbital (LUMO) empowers them with the possibility of undergoing n-doping in the reducing



**Figure 1:** Bis(aryl)acenaphthenequinonediimine

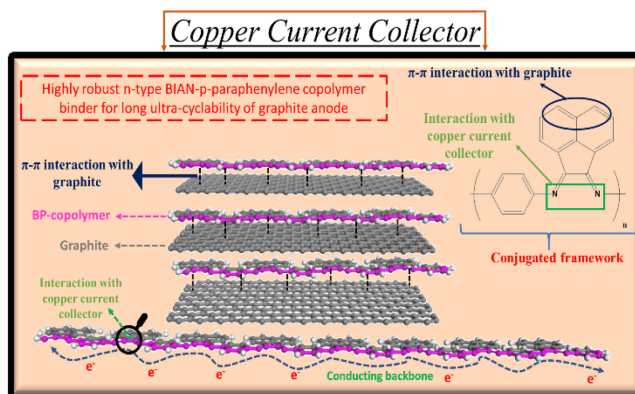


**Figure 2:** Graphical abstract of this dissertation

cathodic environment to restrict the electrolyte decomposition and control the SEI formation if utilized as binders for anodes in LIBs. Therefore, this dissertation work is focused on design, synthesis, and application of novel polymers belonging to the family of compounds bis(aryl)acenaphthenequinone (Ar-BIAN) as binders (Figure 2) to stabilize Li-ion battery (LIB) anodes by the controlled SEI formation, administering mechanical robustness, and maintaining electrical conductivity within the electrode laminate.

## Chapter-2: BIAN-based functional polymer binder to stabilize graphite anode for ultra-long cycling performance.

PVDF has been the conventional polymer binder to stabilize graphite anodes in a LIB. However, because of its non-conducting nature, inability to undergo doping in the cathodic environment to influence the SEI formation, and poor mechanical robustness disqualify it from being a go-to binder choice for ultra-long cycling of graphite anode at a high current rate for future applications. Therefore, this chapter details the design, synthesis, and application of a novel BIAN-p-phenylene (BP) copolymer as binder for graphite in a LIB. The salient

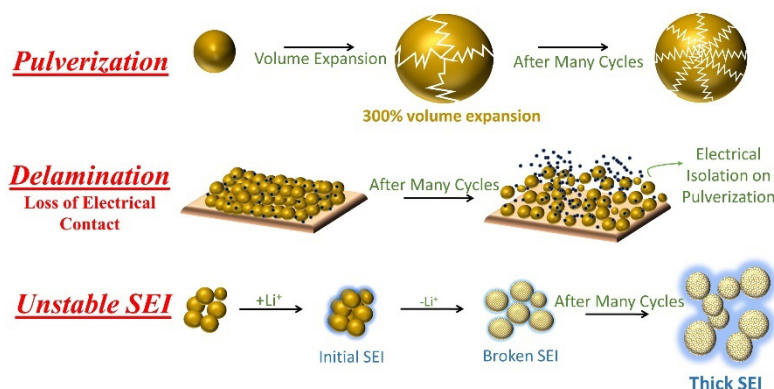


**Figure 3:** Structural significance of BP-copolymer

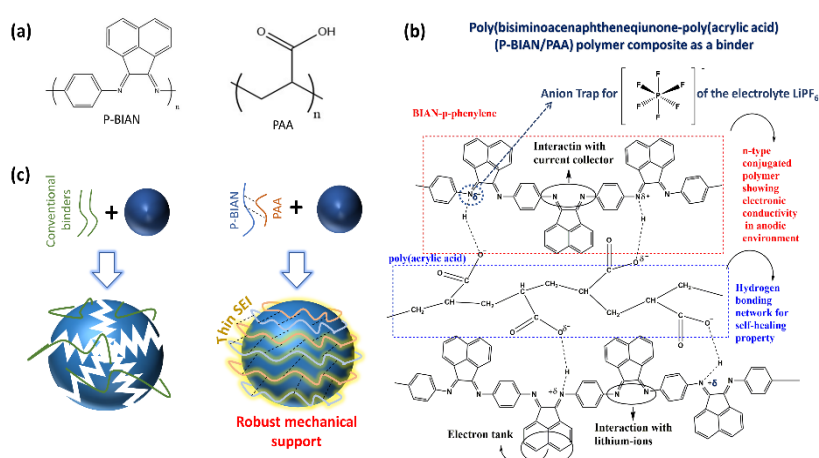
features of BP-copolymer that prove it to be superior to PVDF are (Figure 3): (i) better mechanical robustness (higher Young's modulus), (ii) latching of the electrode laminate on to the current collector through electron rich diimine nitrogen atoms of BP-copolymer, (iii) conjugated framework provides inherent electrical conductivity within the electrode laminate, (iv) its ability to establish tentative  $\pi$ - $\pi$  interaction with graphite framework to administer mechanical robustness, and (v) most importantly, its low-lying LUMO enables it to undergo n-doping in the cathodic environment to restrict the excessive electrolyte decomposition on the anode surface to control the optimal SEI formation. The synergy between all the above-mentioned salient features stabilized the graphite anode in a LIB for over 1700 cycles at a high current rate of 1C with reversible capacity of  $260 \text{ mAhg}^{-1}$  and 95% capacity retention. The anodic half-cells were electrochemically characterized by cyclic voltammetry (CV) studies and dynamic electrochemical impedance spectroscopy (DEIS) studies to understand the interphase formation and its effect on the performance of graphite anode. Further, the postmortem characterization of anodes after electrochemical evaluation was carried out by XPS and FESEM techniques to understand the SEI thickness and surface morphology of the anode.<sup>1</sup>

### Chapter-3: BIAN-based functional n-type conducting self-healing composite binder to stabilize silicon anode in a LIB.

Silicon is potent with 10 times higher gravimetric capacity ( $4200 \text{ mAhg}^{-1}$ ) than the commercial graphite ( $372 \text{ mAhg}^{-1}$ ). Therefore, it is regarded as the next generation anode active materials that can lead to development of LIBs with higher energy density. Also, it can be more economical than graphite because of its natural abundance. However, it has several drawbacks that have hindered its full-scale commercialization in the past decade. The drawbacks are as follows (Figure 4): (i) rapid volume expansion ( $\sim 300\%$ ) on repeated charge-discharge that pulverizes Si particles into smaller fragments, (ii) the pulverization causes loss of interparticle electrical contact and particle to current collector electrical contact, and (iii) continuous decomposition of electrolyte components on the newly pulverized Si surfaces causes thick SEI formation on the anode surface. These drawbacks together destabilize the Si anodes and cause rapid capacity fade with poor cyclability. Therefore, various functional polymer binders that can mitigate these drawbacks have been explored. However, the synthesis of a versatile binder that can collectively mitigate all the drawbacks of silicon anodes is an important area of research. In this regard, this chapter reports the strategic design, synthesis, and application of a novel electrostatically hydrogen bonded P-BIAN/PAA composite binder (Figure 5) that is potent with excellent mechanical robustness, self-healing property, can maintain electrical conductivity within the electrode laminate, and can undergo n-doping by virtue of its low-lying LUMO to restrict the excessive electrolyte decomposition to form a thin SEI. Thus, the silicon anode was stabilized for over 600 cycles of charge-discharge with a high reversible capacity of  $2100 \text{ mAhg}^{-1}$  and 95% capacity retention. The fabricated anodic half-cells were electrochemically characterized by CV and DEIS studies, respectively to understand the interfacial impedance and properties. Also, the electrochemically characterized anodes were subjected to XPS and FESEM techniques to understand the SEI thickness and anode's surface morphology after cycling for over 600 cycles.

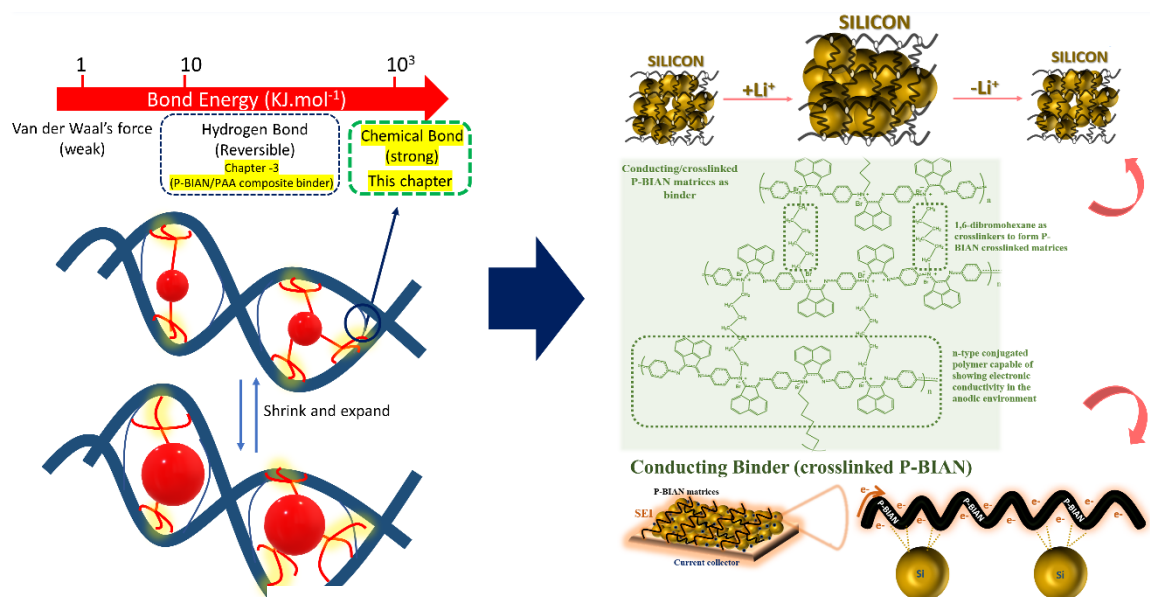


**Figure 4:** Drawbacks associated with Si anodes



**Figure 5:** Structural significance of P-BIAN/PAA polymer composite

## Chapter-4: BIAN-based functional n-type conducting covalently crosslinked composite binder to stabilize silicon anode for ultra-long cycling performance.



**Figure 6:** Structural significance of BP-copolymer

In chapter 3, the electrostatic hydrogen bonding between the P-BIAN and PAA polymeric chains could empower the P-BIAN/PAA composite binder with an ability to stabilize Si anodes. However, for future applications, the demand of LIB with robust and durable cyclability is imminent. Therefore, in Chapter 4, a novel covalently crosslinked P-BIAN polymer matrices were designed, synthesized, and utilized as binder to improve the cyclic stability of Si anodes with higher reversible capacity. The covalently crosslinked P-BIAN binder matrices can restrict drastic volume expansion of Si particles for longtime because of the improved mechanical robustness in comparison to its hydrogen bonded counterpart in chapter 3 as shown in Figure 6. Also, the covalent crosslinking via diimine nitrogen backbone in the P-BIAN would tentatively lower its band energy of LUMO furthermore in comparison to the hydrogen bonded counter in chapter 3. Therefore, by the synergistic effect of its ability to render improved mechanical robustness and n-doping driven SEI formation, Si anodes were stabilized for over 1000 cycles with higher reversible capacity of  $2500 \text{ mAhg}^{-1}$  and 99.1% capacity retention. The fabricated anodic half-cells were electrochemically characterized by CV and DEIS studies, respectively to understand the interfacial impedance and properties. Also, the electrochemically characterized anodes were subjected to XPS and FESEM techniques to understand the SEI thickness and anode's surface morphology after cycling for over 1000 cycles.

**Keywords:** Bisiminoacenaphthene (BIAN), conducting binders, self-healing binders, solid-electrolyte interphase (SEI), silicon anodes, Li-ion batteries.

### Reference:

1. Gupta, A.; Badam, R.; Nag, A.; Kaneko, T.; Matsumi, N., Bis-imino-acenaphthenequinone-Paraphenylene-Type Condensation Copolymer Binder for Ultralong Cyclable Lithium-Ion Rechargeable Batteries. *ACS Applied Energy Materials* **2021**, 4 (3), 2231-2240.

## 論文審査の結果の要旨

本論文では、リチウムイオン二次電池の負極における固体電解質界面の形成制御を指向した BIAN（ビスイミノアセナフテン）構造を有する高分子バインダー材料を設計し、それらの特性を評価している。まず、グラファイト負極バインダーとしての BIAN 型共役系高分子バインダーについて検討した。本ポリマーはアセナフテキノンと p-フェニレンジアミンを酸触媒存在下において重縮合させることにより合成した。本ポリマーにおいては、DFT 計算により電解液のエチレンカーボネートと比較して顕著に LUMO が低く、負極内の還元的環境における共役系高分子の還元ドープにより電導性を発現すると期待された。同時に、その低い LUMO によりエチレンカーボネート（EC）の還元分解に先立って高分子バインダーが還元されるため、EC 由来の固体電解質界面（SEI）を薄く保つことができ、内部抵抗を抑制できると予測された。本ポリマーを負極バインダーとしてアノード型ハーフセルを構築して充放電特性評価を行った。汎用の PVDF をバインダーとした系は 500 サイクル以上の耐久性を示さないが、本系では 1700 サイクル後においても 95%の容量維持率を示した。充放電後の負極を SEM で分析すると、PVDF 系とは対照的に、1700 サイクル後においても微小なクラックが僅かに形成されるにとどまった。加えて、XPS 測定から、サイクル後も内部の構成元素に由来する各ピークが明瞭に観測され、厚い SEI に測定が阻害されていないことから SEI の厚みが抑制されていることが示唆された。

また、BIAN 型共役系高分子バインダーをシリコン負極用バインダーとしても検討した。シリコンは従来系のグラファイトと比して理論容量が 10 倍程度大きく次世代用負極として期待が高いが、同時に充放電中の大幅な体積膨張・収縮により粒子の破断や、集電体からの剥離、粒子の孤立、クラック形成後の連続的な SEI 形成に伴う内部抵抗の減少が問題となっている。本研究では、BIAN 型共役系高分子バインダーをポリアクリル酸とコンポジット形成させ、イミノ基とカルボキシル基との水素結合性ネットワークによる自己修復能により相乗的な安定化効果を期待した。その結果、本系では 600 サイクルまで  $2000 \text{ mAhg}^{-1}$  程度の放電容量を維持することができ、シリコン負極系としては例外的に高い安定性を実現した。

さらに、BIAN 型共役系高分子バインダーを 1,6-ジブロモヘキサンと四級化反応させ架橋高分子バインダーを得た。イオン性部位の導入と架橋による力学的効果により 1000 サイクルにわたって  $2500 \text{ mAhg}^{-1}$  程度の放電容量を維持するに至った。以上のように BIAN 型共役系高分子を活用した負極設計により、各系において電池特性を大幅に改善できることが明らかとなった。これらのバインダー設計戦略は学術的に、実学的に有意義と考えられ博士論文として十分な価値を有すると認めた。