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# Polymer/additive design with BIAN structure to improve properties of electrochemical catalysts and lithium-ion batteries

## Chapter 1: Introduction

Hydrogen energy and lithium-ion batteries (LIBs) will be more widely used from the perspective of environmental issues. Water electrolysis is one of the hydrogen production technologies. The oxygen evolution reaction (OER) is the rate-limiting step in water electrolysis. In this study, we aim to control the electronic structure of  $\text{IrO}_2$  using a conjugated polymer, poly(BIAN-thiophene) to improve the OER catalytic activity. With the increasing demand for LIBs, cathode materials with high working potentials and specific capacities have been actively investigated.  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  electrodes show excellent performance with high reversible capacity at high potentials. However, the organic electrolyte undergoes oxidative degradation the electrode surface at high potentials, resulting in a decrease in capacity and stability. Therefore, in this study, the effect on LIB performance by using BIAN-thiophene as an electrolyte additive was investigated. This additive preferentially decomposes at high potentials and forms a film on the cathode surface.

## Chapter 2: Synthesis of Thiophene Derivatives with BIAN Skeleton

Synthesis of thiophene derivatives with BIAN skeleton (BIAN-thiophene) was carried out. Its application is OER catalysts in water electrolysis and as additives for ternary cathode materials for lithium-ion batteries. BIAN-thiophene was prepared using acetonitrile and methyl 2-aminothiophene-3-carboxylate. The structure of the synthesized BIAN-thiophene was determined by nuclear magnetic resonance analysis and Fourier transform infrared spectroscopy.

## Chapter 3: Control of Electronic Structure of $\text{IrO}_2$ by Conjugated Polymer Support for Highly Efficient Oxygen Evolution Reaction

Novel nanoparticle catalysts with iridium dioxide supported on conjugated polymers were synthesized and their activity and durability against OER.  $\text{IrO}_2/\text{poly}(\text{BIAN-thiophene})/\text{TNT}$  were prepared from iridium complexes and poly(BIAN-thiophene)/TNT by hydrothermal synthesis. The synthesized  $\text{IrO}_2/\text{poly}(\text{BIAN-thiophene})/\text{TNT}$  electrodes were characterized by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, photoelectron spectroscopy, and electrochemical techniques. The binding energy of Ir  $4f_{7/2}$  on  $\text{IrO}_2/\text{poly}(\text{BIAN-thiophene})/\text{TNT}$  was 0.9 eV lower than that of commercial  $\text{IrO}_2$  in XPS measurement. This may be due to the high electron density of Ir due to anchoring of Ir nanoparticles to the polymer via coordination of the nitrogen element. Furthermore, the overpotential of the  $\text{IrO}_2/\text{poly}(\text{BIAN-thiophene})/\text{TNT}$  electrode was 260 mV, which is sufficient for OER activity under acidic conditions.

## Chapter 4: Improvement of Properties of Ternary Cathode Materials for LIB with BIAN-thiophene as an Additive

Use of BIAN-thiophene as an additive for ternary cathode materials for LIBs was examined and its battery performance was evaluated. It is known that electrolyte additives are preferentially oxidized when their HOMO energy level is higher than that of the electrolyte. Since the HOMO energy level of BIAN-thiophene is  $-4.917$  eV, which is higher than that of EC and DEC, it is expected that BIAN-thiophene is preferentially oxidized and the decomposition of organic electrolyte is suppressed. Charge-discharge cycle tests were conducted on cathode-type half cells with  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrodes. The capacity after 100 cycles in the no-additive system dropped to 47 % of the initial discharge capacity, while the system with BIAN thiophene maintained 62 % of the initial discharge capacity after the same cycle.

**Keywords:** Bisiminoacenaphthene (BIAN), oxygen evolution reaction (OER), conjugated polymer, iridium dioxide, Li-ion batteries, electrolyte additive