

# IN-SITU ELECTROCHEMICAL GENERATION OF INITIATOR FOR IONIC POLYMERIZATION

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## INTRODUCTION

Living polymerization is a controlled polymerization process characterized by the absence of chain-terminating and chain-transfer reactions, enabling the precise synthesis of polymers with well-defined molecular weights, narrow molecular weight distributions, and tailored architectures. This technique allows for the creation of block copolymers, gradient copolymers, and complex macromolecular structures by sequentially adding monomers during the reaction. [1] There are three different types of living process that include **anionic polymerization**, cationic polymerization, and radical-mediated processes. The traditional living anionic polymerization processes preferentially involve the use of **lithium-based compounds** such as alkyl lithium [2].

However, their use poses environmental and economic challenges due to the hazardous nature. As a promising alternative, **electrochemical processes** have been explored to initiate and control anionic polymerization in a more environmentally friendly and efficient manner. [3]

## RESEARCH AIM

The aim of this research is the development of an electrochemical and spectroelectrochemical setup on a lab scale for producing a reactive intermediate for living anionic polymerization. We want to investigate the uses of polycyclic aromatic hydrocarbons (PAHS) such as anthracene, naphthalene, and phenanthrene as initiators.

## EXPERIMENTAL SET-UP

Cyclic voltammetry (CV) tests were performed with a potentiostat using a three-electrode cell containing Platinum wire as counter electrode (CE), Ag/AgNO<sub>3</sub> as reference electrode (RE) and Glassy Carbon as working electrode (WE). In this technique, the voltage applied to the working electrode is varied as a cyclic triangular wave, adjusting the scan rate, number of cycles and potential range as required.

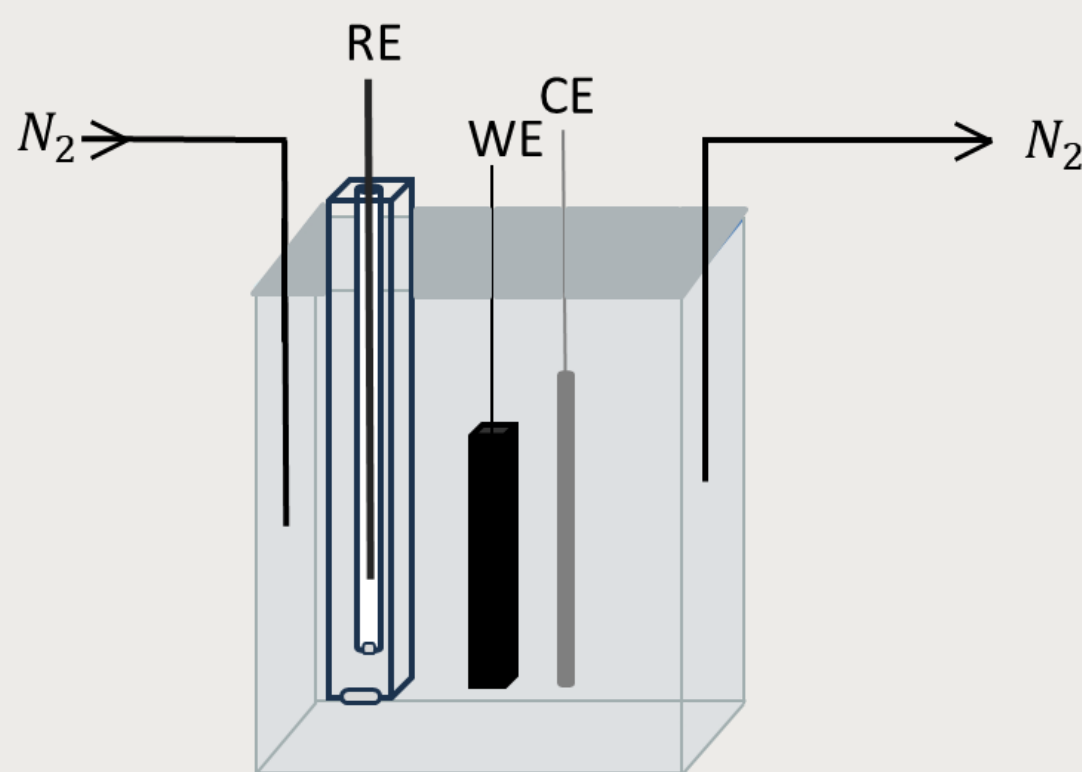


Figure 1- Electrochemical cell set-up on lab scale

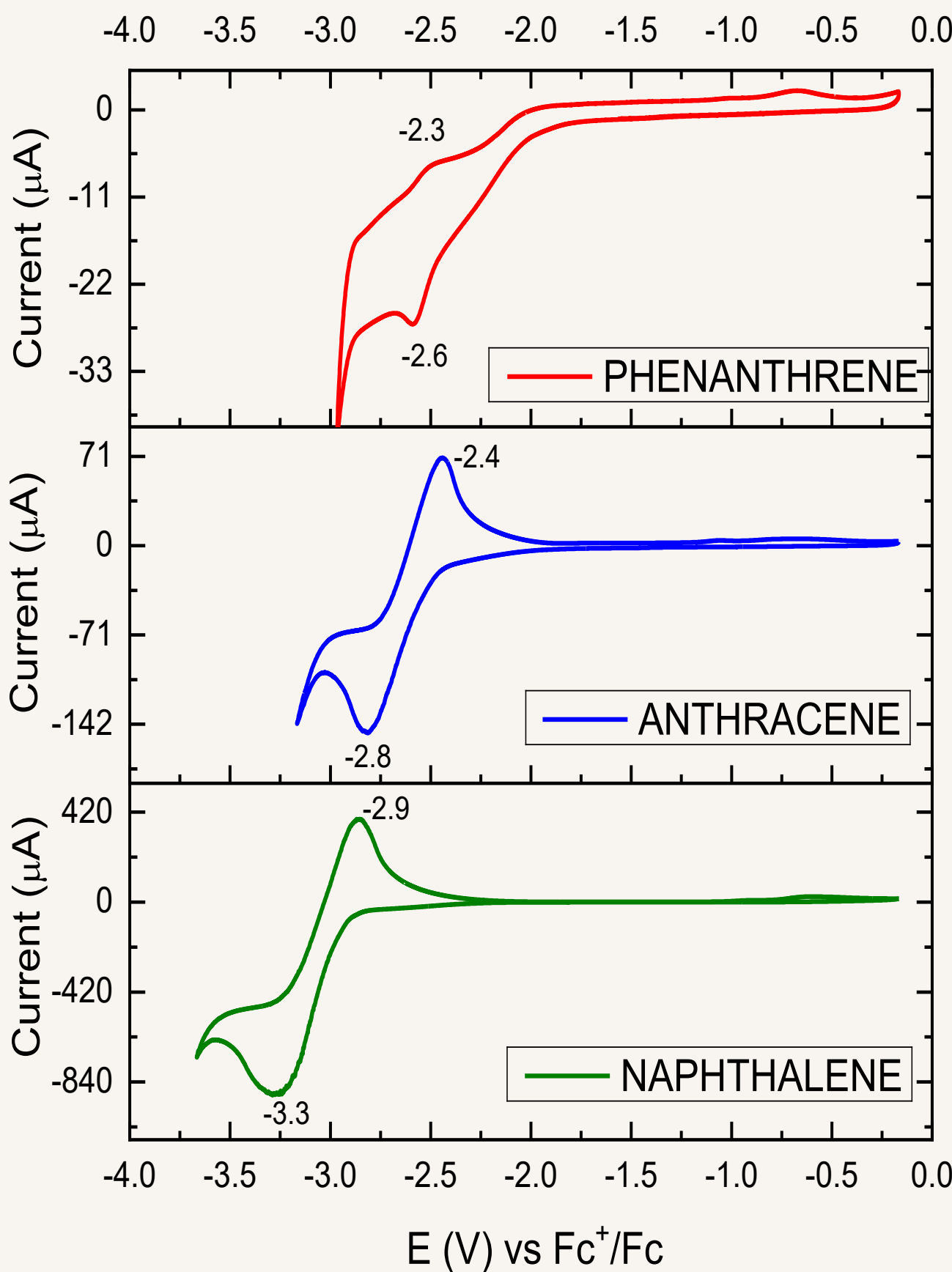
## RESULTS

Two different types of solvents, tetrahydrofuran (THF) and acetonitrile (ACN), were tested. Based on the results obtained, THF appears to be the most promising, as it has shown better performance for carrying out the polymerization. For this reasons we tested different types of support electrolyte.

Solvent	Supporting electrolyte	Usable potential range vs Fc <sup>+</sup> /Fc
THF	n-Bu <sub>4</sub> NPF <sub>6</sub>	From -3.5 to 0 V
	NaBPh <sub>4</sub>	From -2.0 to 0 V
	LiClO <sub>4</sub>	From -1.2 to 0 V
	LiCl	X
	LiBF <sub>4</sub>	X

We obtain that the better solvent-supporting electrolyte pair is THF - n-Bu<sub>4</sub>NPF<sub>6</sub> because it has a broader potential window. Then with these operation conditions we made the first electrochemistry studies with the PAHS which are characterised by increasing conjugation system. [4]

After electrochemical and spectroelectrochemical analyses we observed that anthracene forms a reactive intermediate, the radical anion, which can initiate the polymerization process in the presence of a specific monomer.



## CONCLUSIONS

- We have identified the experimental set-up and the operating conditions for carrying out the electrochemical analyses.
- We have demonstrated the generation of the reactive intermediate through electrochemical and spectroelectrochemical analyses.

## FUTURE PERSPECTIVES

- Studies other PAHS and α-olefins as initiators.
- Perform polymerization tests to obtain polymeric material with different characteristics and varying molecular weights.

### References

[1] Szwarc, M. Living Polymers and Mechanisms of Anionic Polymerization, 1st ed.; Advances in polymer science; Springer: Berlin, **1983**; Vol. 49.  
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[4] Ripani, L.; Bombonato, E.; Paolucci, F.; Marcaccio, M. Electron Transfer in Polyaromatic Hydrocarbons and Molecular Carbon Nanostructures. Curr. Opin. Electrochem. **2022**, 35, 101065.