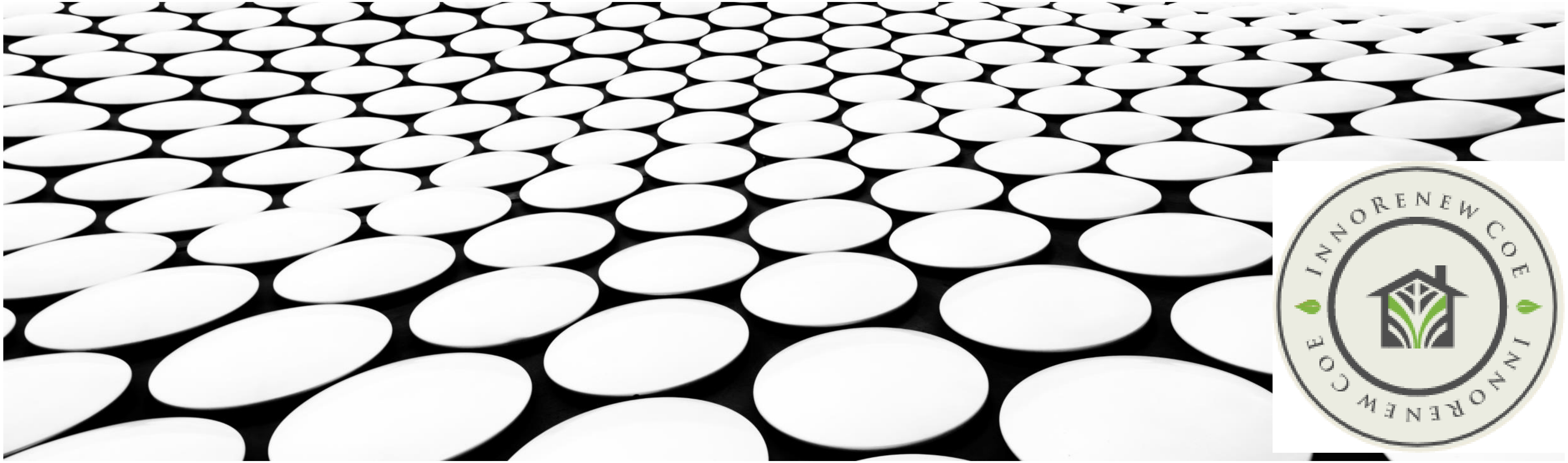
MULTISCALE MODELLING STUDIES OF EXPLORING LIGNOCELLULOSIC BIOMASS

VEERAPANDIAN PONNUCHAMY



04. 11. 2020

OUTLINE

- What is research?
  - Develop a research project, type of research, research process …
- Multiscale modelling – Background
- Example projects

A SHORT BIO

Masters in Chemistry - India

2011

PhD in Physics

“Electrolytes for Lithium-ion batteries”

2011 - 2015

Research Associate

“Lubricants for automobiles”

2015 - 2018

Researcher

“Multiscale Modelling investigation of wood and its components”

2019 -

WHAT IS RESEARCH ?

- Art of scientific investigation
- Research is an organized and systematic way to find answers to questions
- Research is a creative process, addition to the available knowledge – for further advancement

SEARCH for knowledge through clear OBJECTIVES & SYSTEMATIC methods to obtain solution to a problem

PURPOSE OF RESEARCH

- Review or synthesis existing knowledge
- Investigate existing situations or problems
- Provide solution to problems
- Construct or create new procedures or systems
- Explain new phenomenon
- Generate new knowledge

HOW TO DEVELOP A GOOD RESEARCH QUESTIONS?

FINER method

Feasible	Interesting	Novel	Ethical	Relevant
Subjects Resources Manageable ? Data available?	Interesting	In relation to previous findings Confirm or refute? New setting or new model?	Social or scientific value? Safe?	Advance scientific knowledge? Impact society policy? Guide future research?

RESEARCH METHODS VS RESEARCH METHODOLOGY

- **Research Methods** are the methods that the researcher adopts for conducting the research Studies
  - In other words, all those methods which are used by the researcher during the course of studying his research problem are termed as research methods.

- **Research Methodology** is the way in which research problems are solved systematically.
  - we study the various steps that are generally adopted by a researcher in studying his/her research problem along with the logic behind them
  - May differ problem to problem

It is the Science of studying how research is conducted Scientifically

TYPES OF RESEARCH

Applied

It aims at finding a solution for an immediate problem facing a society or an industrial/business organisation

→ Case study
→ Comparison

Basic/Fundamental

It is mainly concerned with generalisations and with the formulation of a theory.

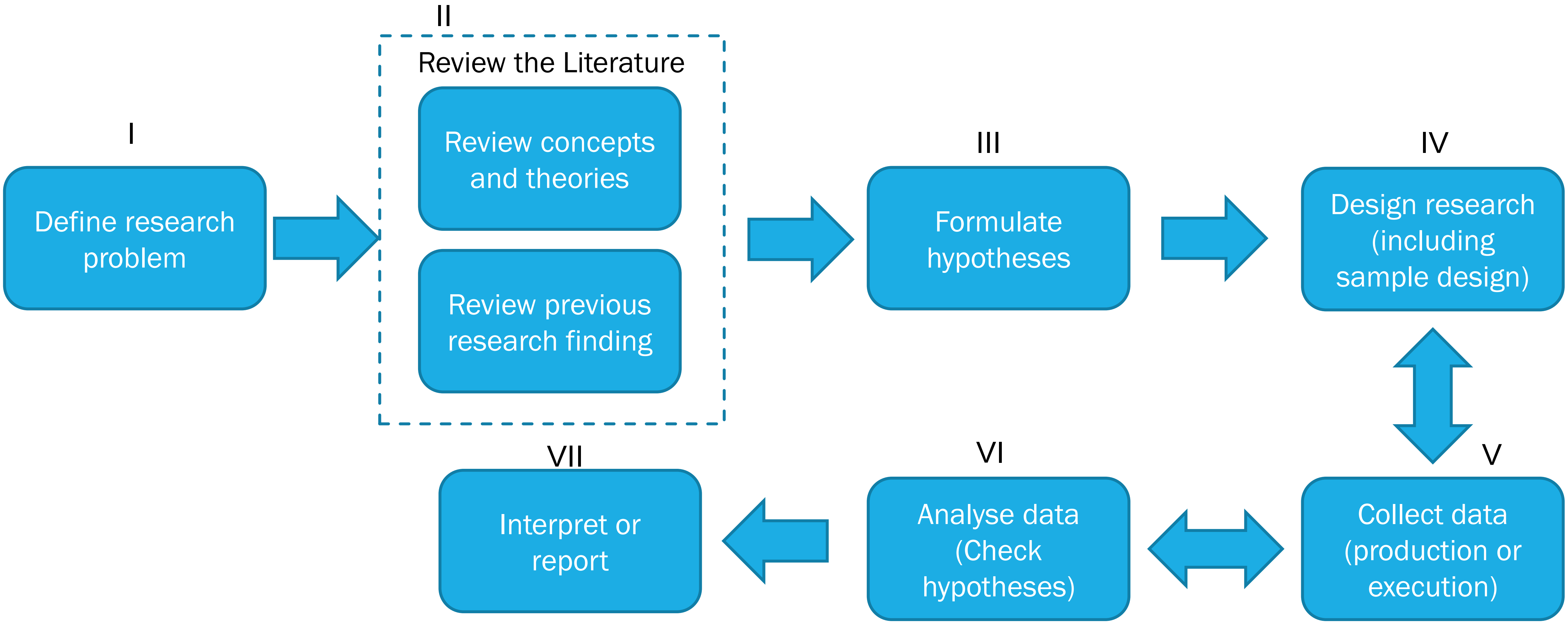
→ Correlation-prediction
→ Theory construction
→ Towards finding information – has a broad applications

Business

→ Analysis
→ Evaluation
→ Design-demonstration
→ Status

Research approaches: Qualitative and Quantitative

FLOW CHART OF RESEARCH PROCESS



RESEARCH OVERVIEW

1. Introduction
   - Introducing research problem
   - Introduction of objectives and how objectives will be achieved
2. Literature review
   - Review of previous work relating to research (define, explain, justify)
   - Review of previous work relating to methodology
   - Review previous work relating to results
3. Methods
   - Explanation of how data was collected and generated
   - Explanation of how data was analysed

RESEARCH OVERVIEW

4. Results and Findings

- Presentation of results
- Interpretation of results

5. Discussion and Conclusion

- Discussion of result - comparison with results in previous research, effect of method used
- Has the research problem been solved?
- To what extent has the objective being achieved?
- What has been learnt from the results?
- How can this knowledge be used?
- What are the shortcomings of the research or research methodology?

CONCLUSION

- ✓ A good research is Systematic, Logical, Empirical, Replicable
- ✓ Bear in mind the purpose of the work and method
- ✓ Keep notes what you did and what happened – Make sure you develop some way of recording your work & carefully select which materials to include in your methodological section
- ✓ Do not include unnecessary details
- ✓ Avoid using “I” write about what you did and sometime avoid “we” too. Use passive voice for writing and be consistent

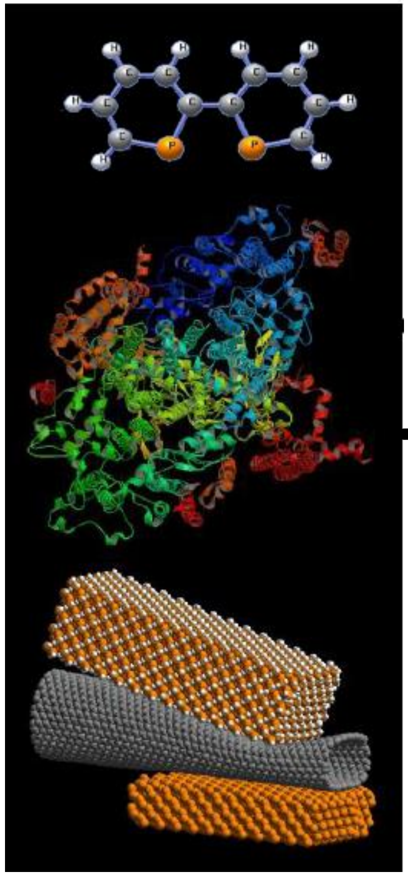
EXAMPLES OF RESEARCH DESIGN

COMPUTATIONAL CHEMISTRY (MULTISCALE MODELLING)
(BACKGROUND)

WHAT IS MULTISCALE MODELLING

Solving chemical problems with numerical experiments

OBJECTS
Molecular systems



TOOLS
Models

Physical laws

Atomic and molecular interactions

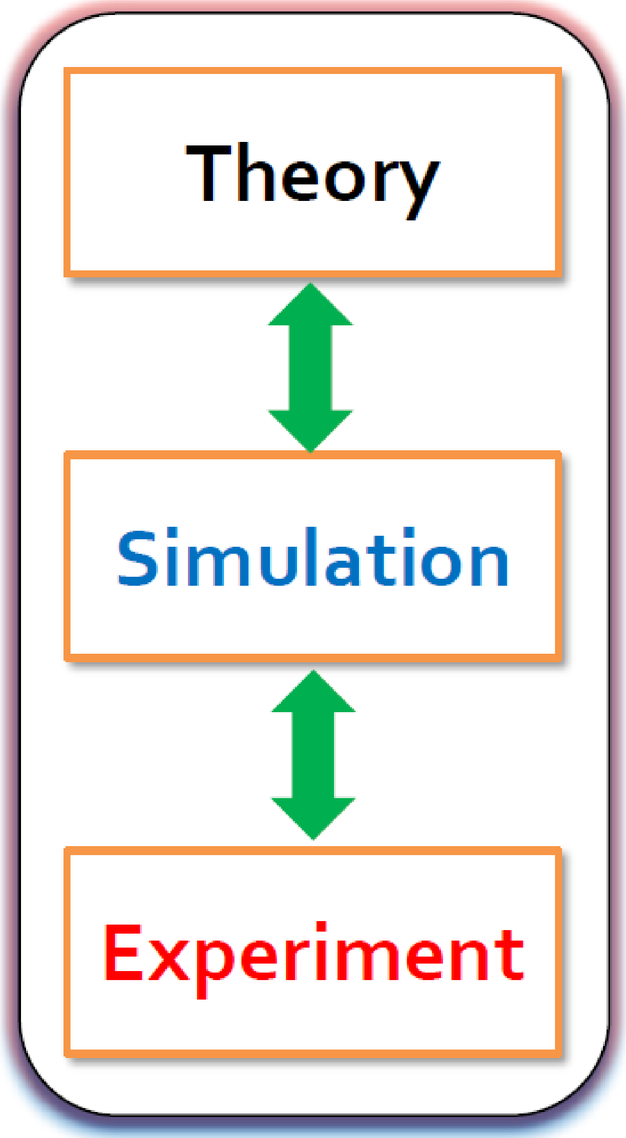
Mathematical models

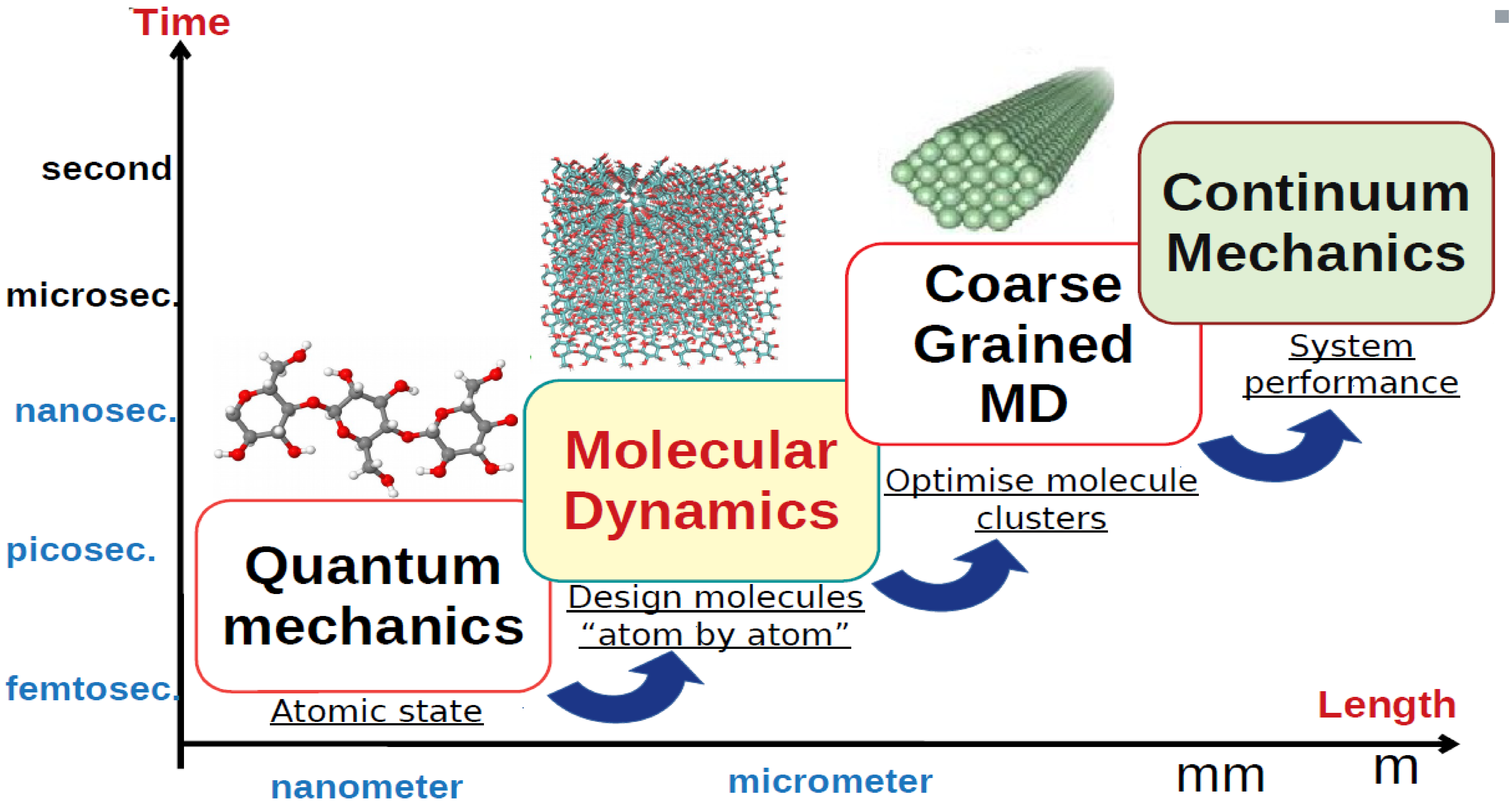
GOALS
Properties
Comparison
Theory/Experiments

Geometries
Spectra
Thermodynamics
Activation energies
Rate constants

WHY DO WE NEED SIMULATIONS?

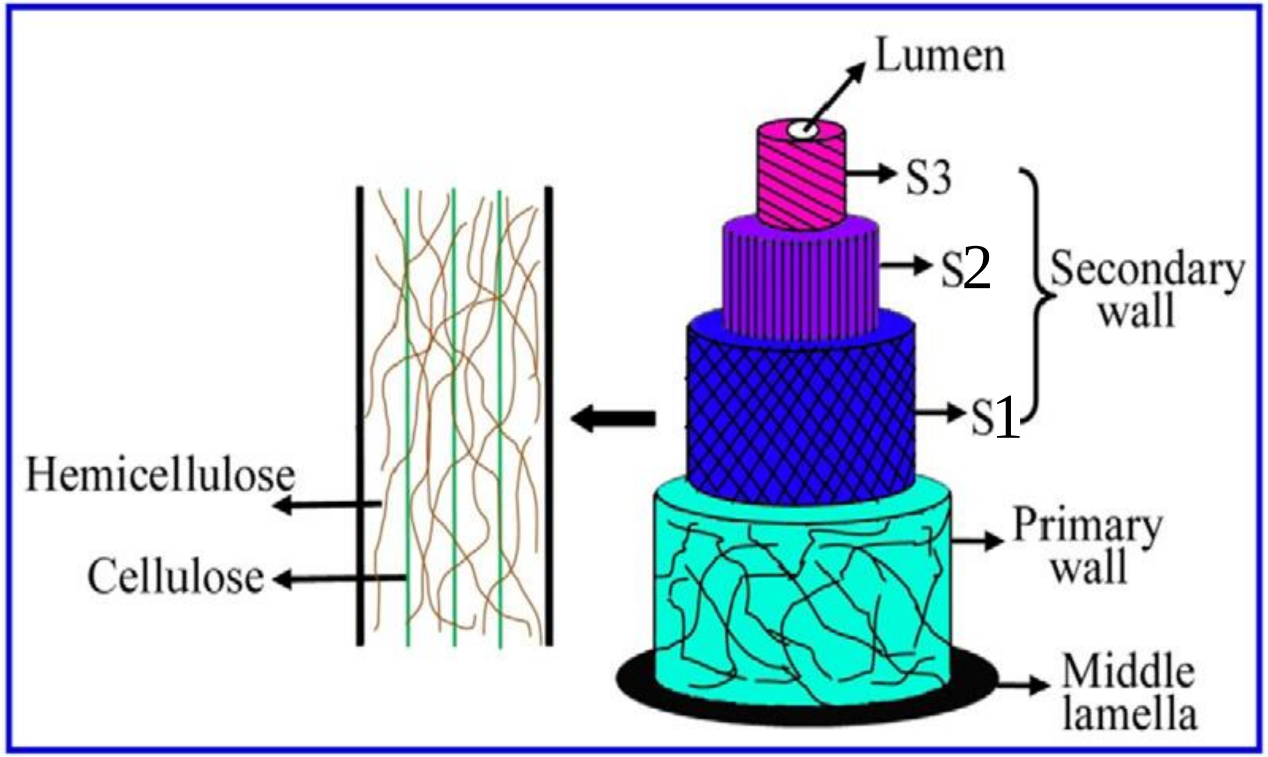
- In most cases, experiments are:
  - Difficult or impossible to perform
  - Too dangerous perform
  - Expensive and time consuming
  - Blind and too many parameters to control
- Simulation is a powerful tool:
  - Replace or explain and understand experiment
  - Bridge between theory and experiment
  - Get the properties of materials at atomic or molecular level
  - Behavior of materials on different time-and length-scales
- Can be applied in, but not limited to:
  - Physics and Applied Physics
  - Chemistry
  - Materials and Engineering



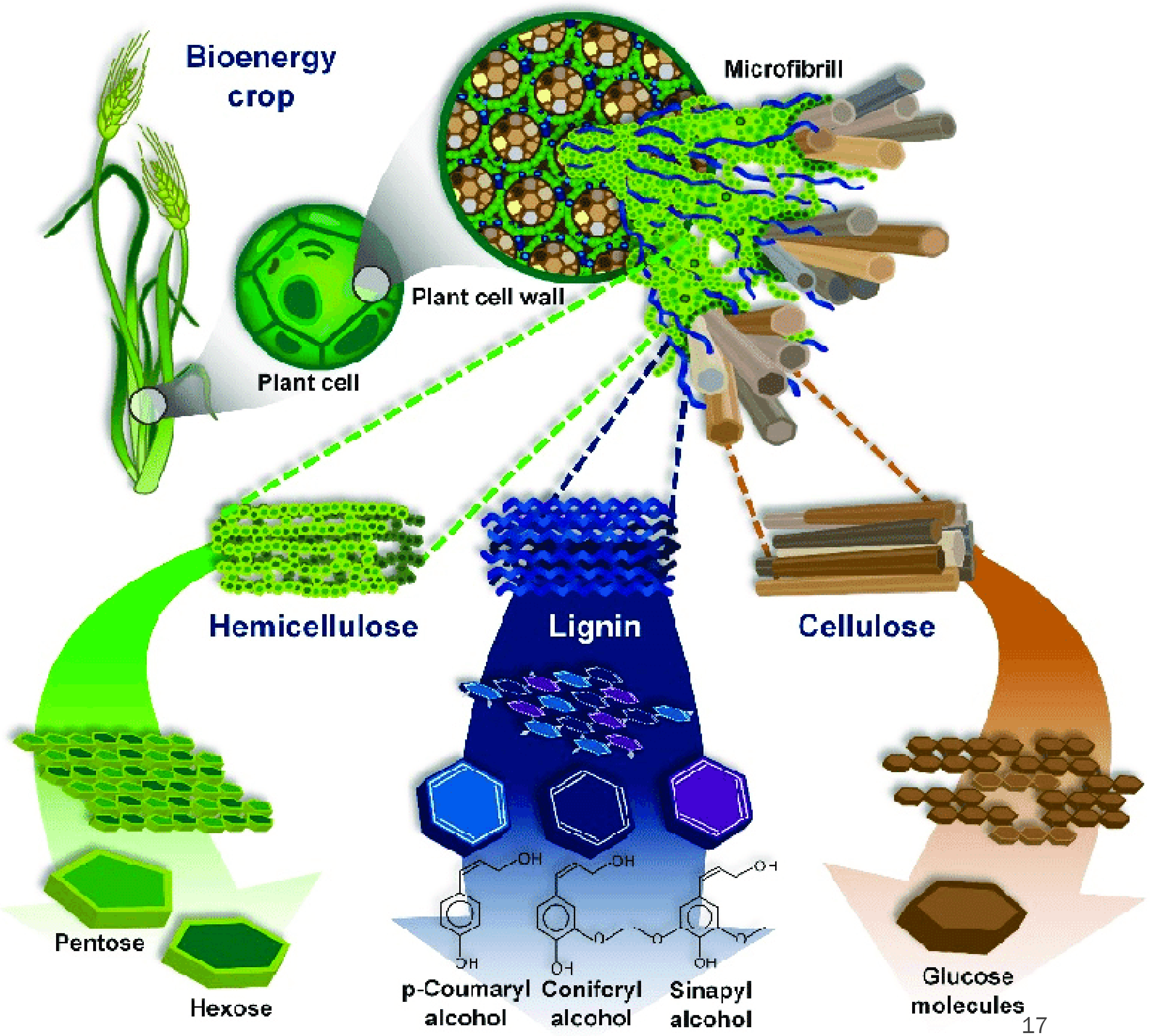

Time
second
microsec.
nanosec.
picosec.
femtosec.
Quantum mechanics
Atomic state
Molecular Dynamics
Design molecules "atom by atom"
Coarse Grained MD
Optimise molecule clusters
Continuum Mechanics
System performance
Length
nanometer
micrometer
mm
m

EXAMPLE 1 – WOOD MODIFICATION

HIERARCHICAL STRUCTURE OF A WOOD CELL WALL



LIGNOCELLULOSIC BIOMASS



Appl. Sci. **2019**, *9*(18), 3721

INTRODUCTION

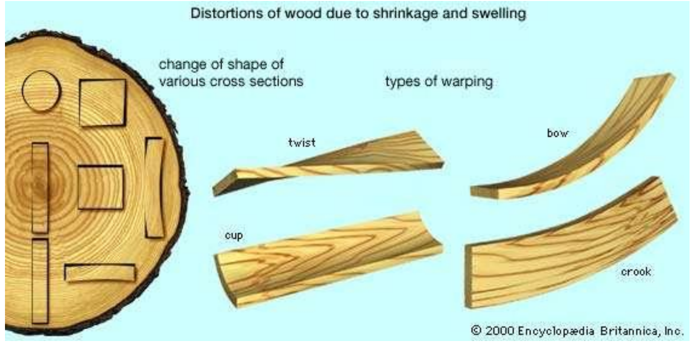
Wood

→ a highly abundant and sustainable construction material

→ used for designing of new building structures, façades, furnishings, windows

→ anisotropic material and has a strong tendency for absorbing water

→ causes changes in mechanical properties, dimensional stability, durability etc



How to improve the properties of wood?

https://www.britannica.com/science/wood-plant-tissue/Hygroscopicity
https://www.remingtonlights.com/wood-furniture-an-uncommon-bit-of-furnishing.html

WOOD MODIFICATION

- Improving the durability – increasing the resitance against biological attack
- Improving the dimensional stability and hygroscopicity
- Hardness
- Aesthetic (color)
- Acoustic properties

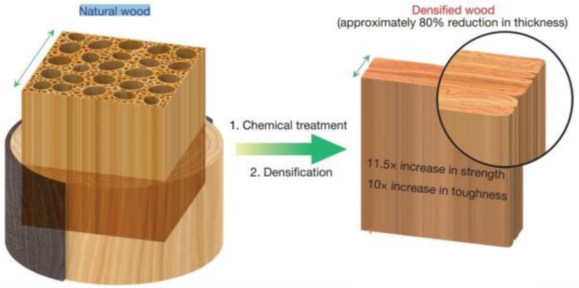
Thermal

Different modification process

- ✓ Thermal treatment
- ✓ Chemical modification
- ✓ Thermo-hydro-mechanical processes
- ✓ Surface treatments
- ✓ Hybrid modification

Chemical Modification

Hybrid modification



CHEMICAL MODIFICATION OF WOOD

Chemical alteration of cell wall polymers

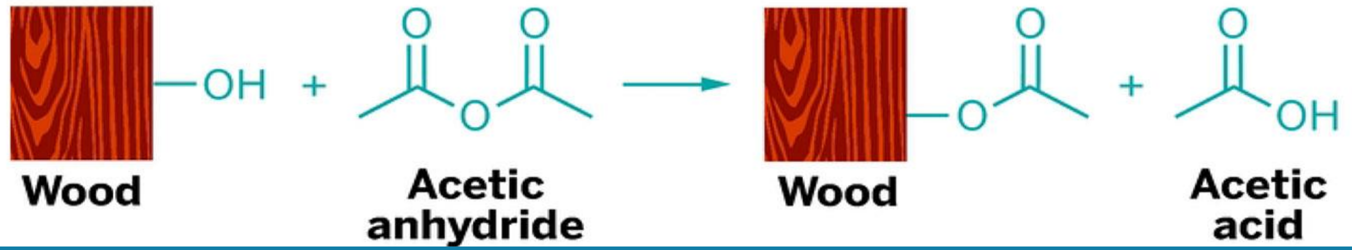
- Reaction with wood polymers
- Cross linking
- Degradation of cell wall

Active modification processes

- Acetylation
- Furfurylation
- DMDHEU based modification
- Silicate / silane-based process

Acetylation of wood

- Acetylation changes free hydroxyl in wood into stable and moisture resistant acetyl groups
- Reduction in water content → dimensional stability
- Improves durability, coating performance and extend functional service life



NO concrete information are available for the reactivity of wood polymers?

DESIGNING OF OBJECTIVES

- ❑ How acetic anhydride molecule approaches the wood polymers (cellulose and lignin)?
- ❑ What about the strength?
- ❑ What is the driving force for wood modification?

NO PRIOR research has been performed for wood modification using multiscale modelling techniques

RESEARCH METHODS

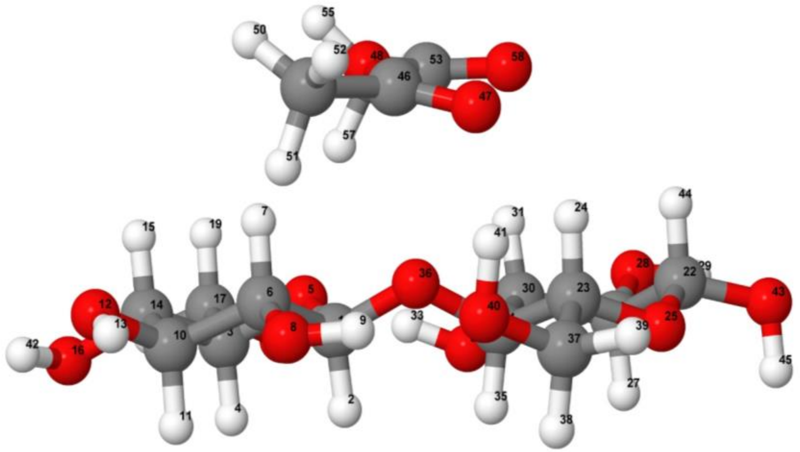
- ❑ Using Multiscale modelling techniques

RESEARCH METHODOLOGY

- ❑ Interaction energy calculation – Provide the strength of interaction between wood polymers with acetic anhydride (**Quantitative**)
- ❑ Hydrogen bonding predictions – Give insights for driving force which influence the rate of acetylation reaction (**Quantitative**)

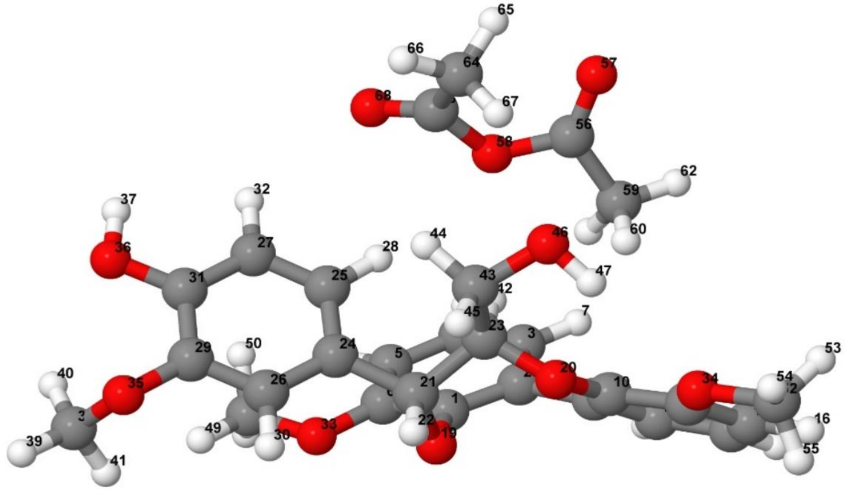
RESULTS

Cellobiose-Acetic anhydride



	H-bond	Length (Å)	ΔE (kJ mol-1)
Cellobiose-AA	O47 - H41	1.88	-81.48
	O58 - H24	2.50	
	O48 - H7	2.63	
Lignin-AA	H67 - O46	2.39	-61.69
	H60 - O46	2.63	
	O58 - H42	2.63	
	O68 - H28	2.72	

Lignin-Acetic anhydride



Interaction energy

$$\Delta E = 2625.5 \times (E_{ab} - E_a - E_b)$$

$$kJ\ mol^{-1}$$

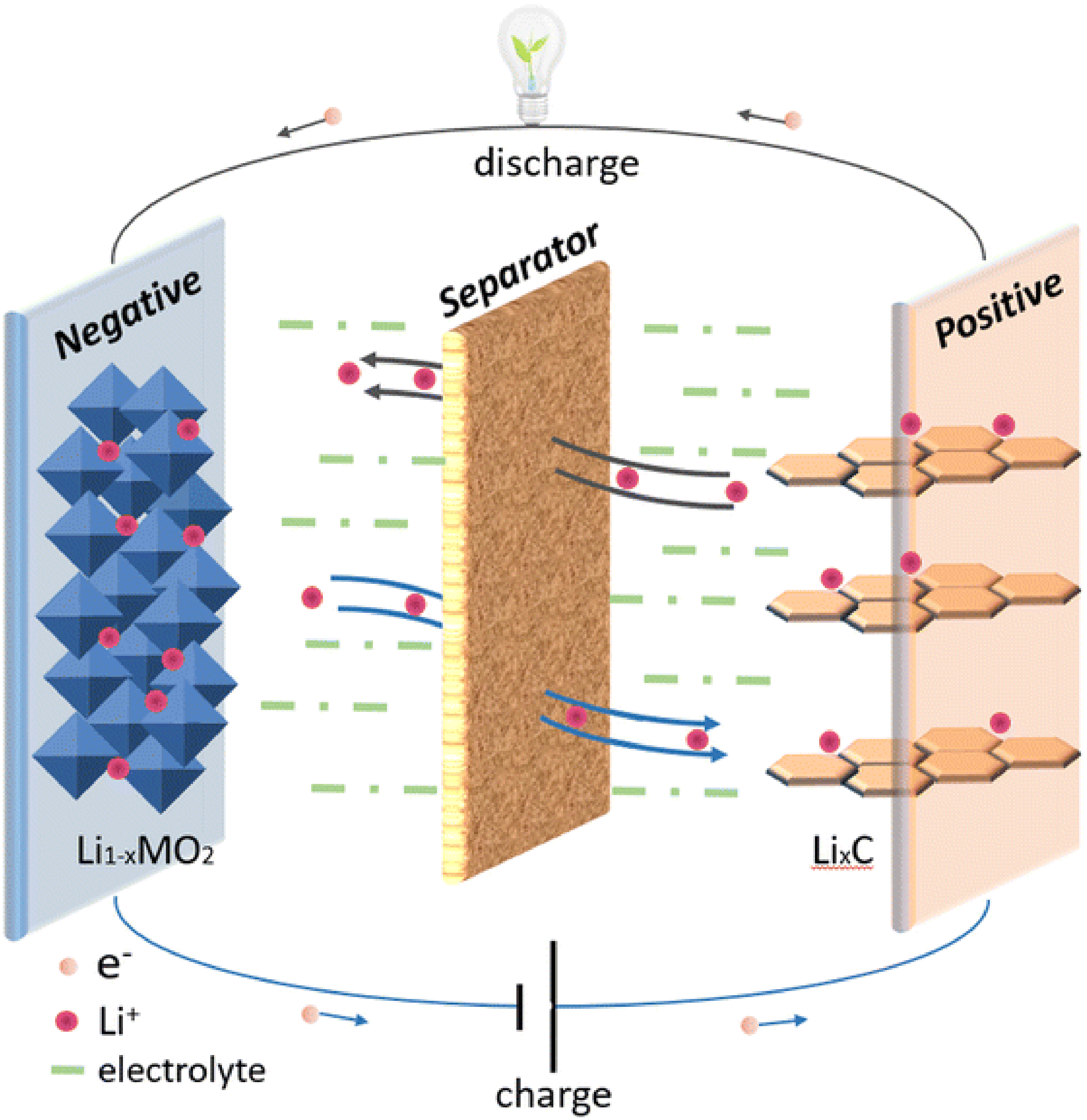
Cellulose strongly interacts with acetic anhydride

CONCLUSIONS

- The calculated interaction energy is higher for cellobiose-acetic anhydride than lignin-acetic anhydride (about 20 kJ mol^{-1}) → acetic anhydride easily approaches cellulose hydroxyl groups over lignin
- Hydrogen bond result demonstrates → electron density and its Laplacian for cellobiose-acetic anhydride are significantly higher than lignin-acetic anhydride
- **Experiments**: lignin is highly reactive towards acetylation
- The obtained results were only related to the investigated lignin model, and the results can differ for other lignin model compounds
- Results for crystalline cellulose model can be different

EXAMPLE 2

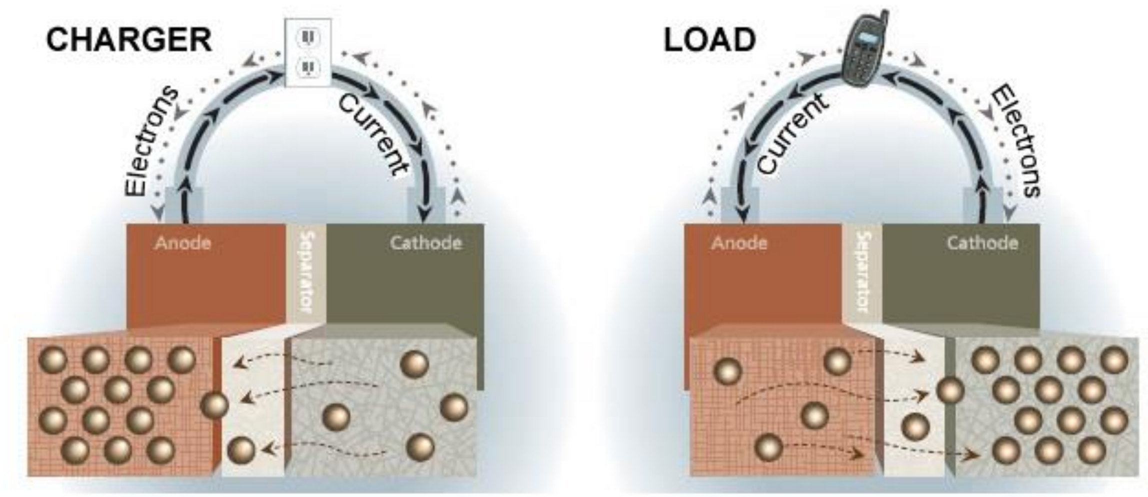
CELLULOSE/POLYMERS BASED COMPOSITE MEMBRANE FOR THE DEVELOPMENT OF HIGH-PERFORMANCE LITHIUM-ION BATTERY SEPARATOR



INTRODUCTION

Lithium batteries are more robust devices

- ✓ Predominantly occupies portable electronics
- ✓ Emerging fields: low-emission vehicles and energy storage systems



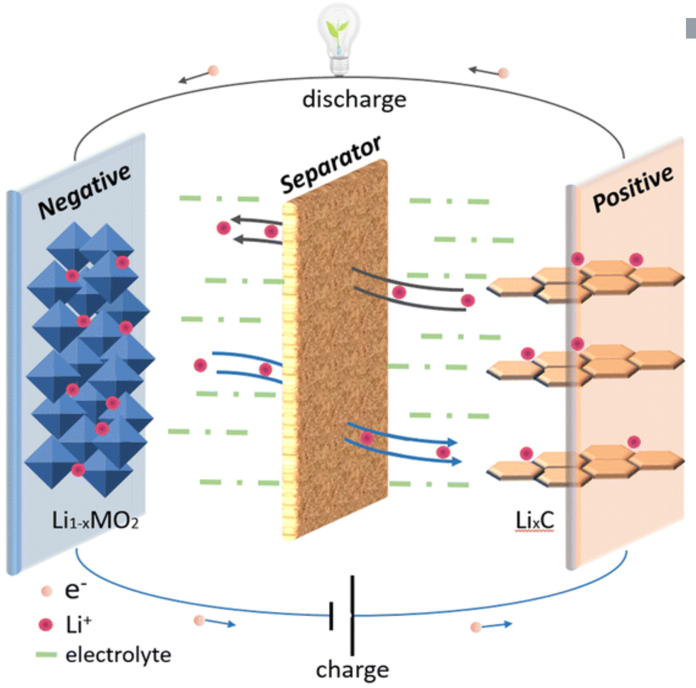
Lithium-ion Rechargeable Battery
Charge Mechanism

Lithium-ion Rechargeable Battery
Discharge Mechanism

WHAT IS SEPARATOR IN BATTERIES?

- Cathode and Anode are isolated by a "Separator"
- Separator is moistened with electrolyte and promotes the movement of ions between anode and cathode
- Separator is an isolator and no electrical conductivity
- 3 percent of the cell content

Asahi Kasei company (Japan) invests $268m into battery separator production



SEPARATOR MATERIALS

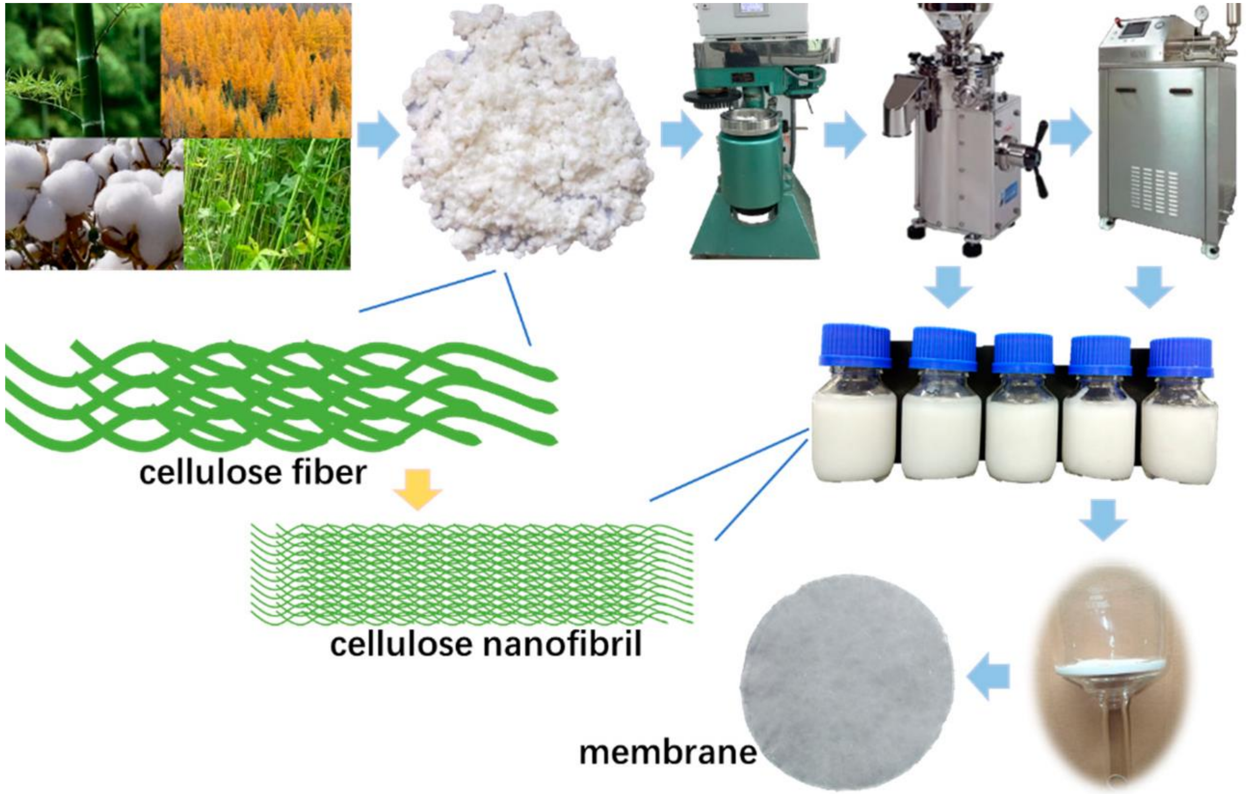
Early separators were made of

- Rubber
- glass fibre mat
- cellulose
- polyethylene plastic – used in commercially available Li-ion batteries – In our mobile phones

- Wood was the original choice but it deteriorated in the electrolyte.

CELLULOSE SEPARATORS FOR LITHIUM-ION BATTERY

- ➢ Bamboo pulp
- ➢ Hardwood pulp
- ➢ Softwood pulp
- ➢ Cotton pulp
- ➢ Hemp pulp



- ✓ Hemp pulp and hardwood pulp - the best wettability - suitable for coating of composite LIB separators
- ✓ Softwood pulp and cotton - best tensile strength - matrix material of cellulose LIB separators

Materials ***2019***, *12, 2*

DEVELOPMENT OF RESEARCH IDEAS FOR MULTISCALE MODELLING

materials

MDPI

Review

Bio-Based Polymer Electrolytes for Electrochemical Devices: Insight into the Ionic Conductivity Performance

Marwah Rayung [1], Min Min Aung [1,2,*], Shah Christirani Azhar [2], Luqman Chuah Abdullah [3], Mohd Sukor Su'ait [4], Azizan Ahmad [4,5] and Siti Nurul Ain Md Jamil [2]

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5 School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Malaysia
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Received: 10 October 2019; Accepted: 4 December 2019; Published: 12 February 2020

check for updates

4. Summary and Outlook

Based on the literature available to date, a variety of bio-polymers have been explored by researchers, and the number of studies keeps on expanding, particularly over the last few decades. Similar to conventional petrochemical-based polymer electrolytes, bio-based polymers also suffer from low ionic conductivity when compared to liquid electrolytes. In fact, many studies have attempted to address this limitation. Researchers have suggested a number of ways to tackle this shortcoming by introducing fillers, plasticizers, and polymer blending methods. Nevertheless, the literature is still lacking in terms of the evaluation of the shelf life performance of bio-based electrolytes. This is another point of view that demands further investigation. As for applications, some of the bio-based polymer electrolytes have been tested in dye-sensitized solar cells, super-capacitors, and batteries. Despite the various types of bio-based materials that have been investigated as polymer electrolytes, they have yet to attain the status of commercial viability. Hence, extensive studies are still required to develop a system to achieve a level of performance that is comparable to the conventional liquid electrolytes. One interesting approach is to use computational and molecular modeling to understand the fundamental aspects of the materials. Such tools will provide important information, especially on the conduction mechanism, and can be used to assist and support the interpretation of experiments. Future work in this area will be very interesting as it will provide an in-depth understanding of the theoretical principle of the polymer electrolyte. From the preceding review, proper designs based on carefully selected materials and methods are expected to improve the bio-based polymer electrolytes performance.

LITERATURE REVIEW

Cellulose/PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropylene)) composite

Compared to the PP separator, the cellulose/PVDF-HFP composite separator possesses

- ✓ higher ionic conductivity
- ✓ better electrolyte uptake
- ✓ superior thermal resistance
- ✓ enhanced electrochemically interfacial stability

Table 1. Physical Properties of the Cellulose-Based Separators

sample	thickness (μm)	porosity (%)	Gurley value (s)	Gurley value (200 °C) (s)	electrolyte uptake (%)
PP separator[a]	25	55	235		120
cellulose nonwoven	25	75	6.6	6.6	340
cellulose/PVDF-HFP	27	65	32.7	36	280

[a]PP separator is melted at 165 °C.

From extensive literature search – NO research work has been reported with modelling techniques

ACS Appl. Mater. Interfaces 2013, 5, 128−134

GAP ANALYSIS

Cellulose/PVDF

+ High mechanical strength
+ Good affinity to electrolyte
+ Excellent thermal stability
+ Excellent wettability
- Experience in poor ionic conductivity: no concrete information available
- No study exists in molecular modelling

This PROJECT will focus

➢ **Designing of PVDF polymer**
➢ **Development of Cellulose:PVDF**
➢ **Designing of gel polymer electrolyte (GPE)-Cellulose:PVDF/$LiPF_6$-EC:DMC**
➢ **Investigation of electrode/GPE interphase with different potential**

This PROJECT will achieve

+ Key interaction between cellulose-PVDF
+ Provide underlying mechanism of ionic conductivity of GPE
+ Impact of electrode for Li-ion transport in GPE
+ **Guide the material and device design for experiments**

OBJECTIVES

- Perform an in-depth analysis of the physico-chemical and mechanical properties of cellulose-PVDF system to understand its interactions without presence of electrolyte
- Develop an efficient and reliable model of cellulose-PVDF with $LiPF_6$ – EC:DMC (1:1) for optimization of different components with concentration
- Evaluate the designed cellulose-based polymer electrolyte under electric field to elucidate the electrode/electrolyte interphase to assess the compatibility

RESEARCH METHODS

- ❑ Using Multiscale modelling techniques

RESEARCH METHODOLOGY

- ❑ Mechanical property calculation of cellulose/PVDF – Provide key interactions between cellulose and PVDF polymer (both **Qualitative and Quantitative**)
- ❑ Lithium ion transport calculations – Give insights for better performance of novel materials (**Quantitative**)
- ❑ Presence of electric field – Device design (Mimic real device)

TO BE PERFORMED…

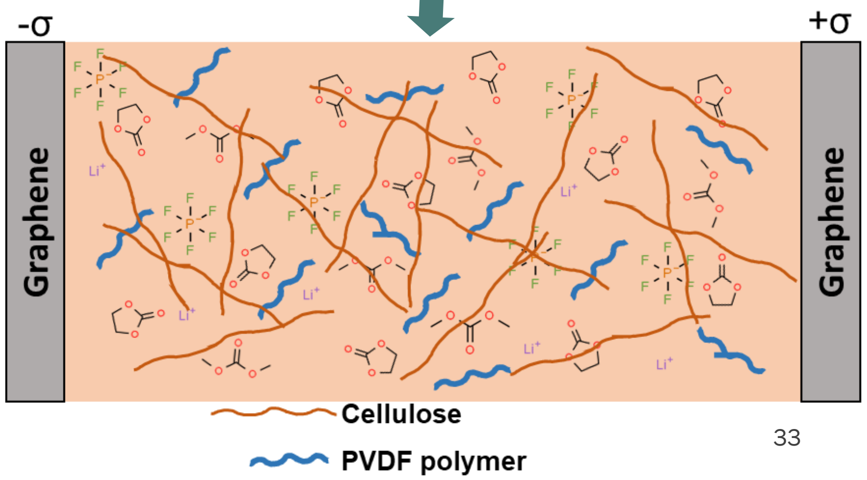
O1: Development of Cellulose-PVDF system

↓

O2: Development of Cellulose:PVDF/$LiPF_6$-EC:DMC

↓

O3: Electrode-Electrolyte interphase: Impact of electric field on the Polymer Electrolyte



FINDING RESEARCH IDEAS - POSSIBILITIES

- ❑ Create your own idea/propose/hypothesis – Extensive literature search is necessary – TAKE extra time for creating objectives to avoid repetition

- ❑ READ recent review articles in your fields – mainly sections “Future challenges” “Outlook” “Conclusions” – to create some ideas

WEBSITES FOR LITERATURE SEARCH

Google scholar (https://scholar.google.com)
Science direct (http://www.sciencedirect.com/)
Pubmed (https://pubmed.ncbi.nlm.nih.gov/)
Scopus (https://www.scopus.com)
Web of science (https://clarivate.com/webofsciencegroup/solutions/web-of-science/)
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THANK YOU FOR YOUR ATTENTION

QUESTIONS??