

LITHIUM ION BATTERY PERFORMANCE ENHANCEMENT BY SURFACE COATING

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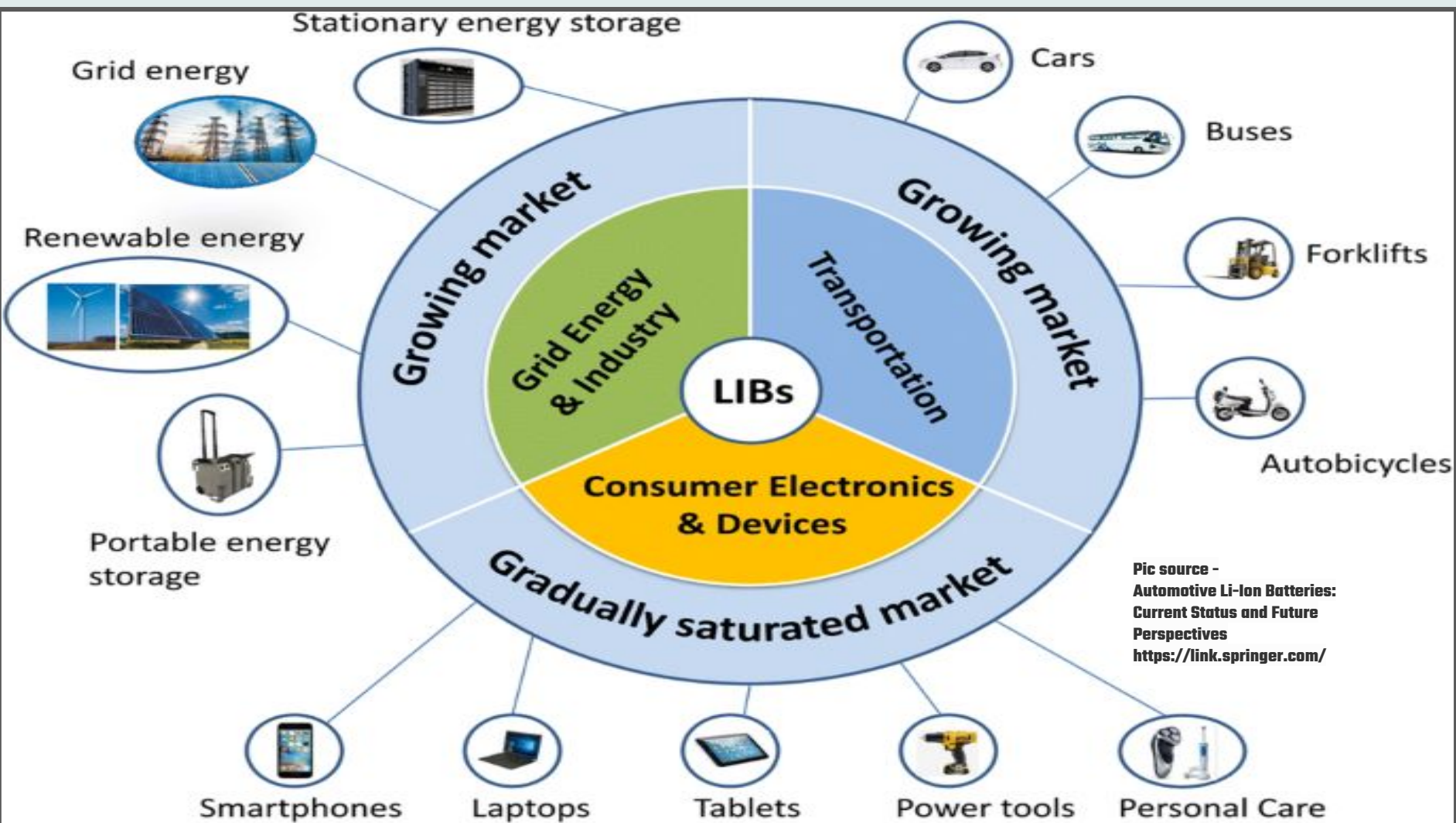




01

WHAT & WHY?

Introduction to
problem statement



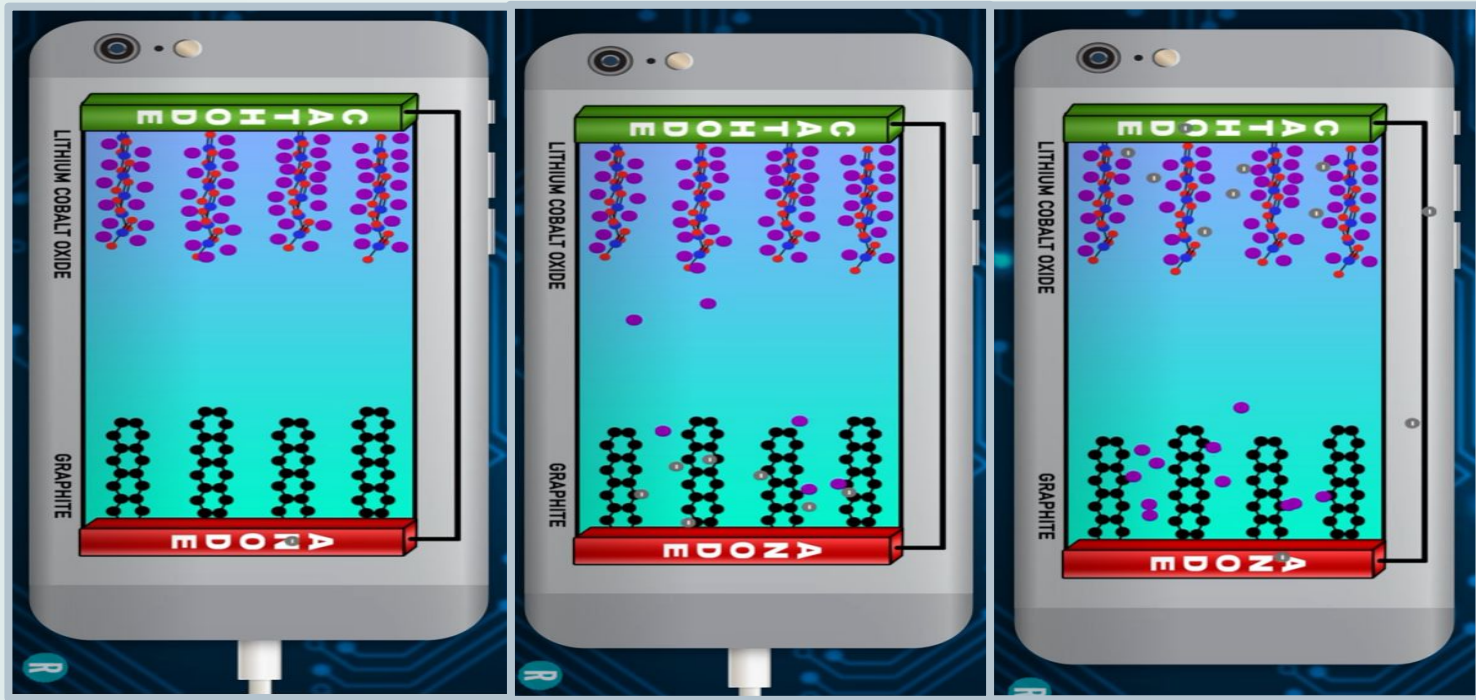


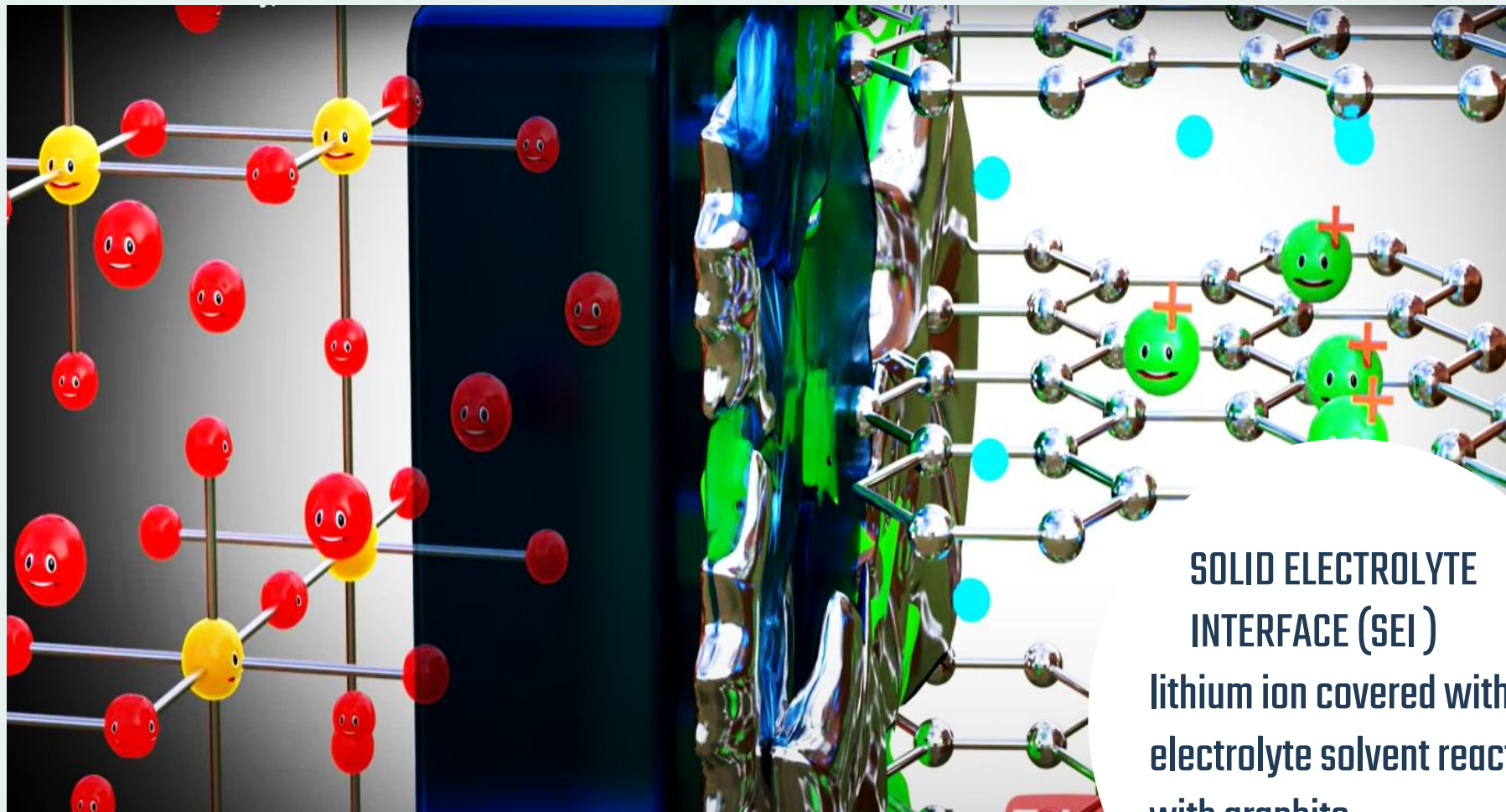
BACKGROUND



- From automobiles to earbuds, Lithium ion batteries are ubiquitous
- Yet, they have not found the success they can bring about - Insufficient life, low abuse tolerance, Safety & stability in certain conditions, high cost
- This is due to low energy density, wearing out of cathode, side reactions, elevated temperatures/ heat

HOW LITHIUM ION BATTERY WORKS ?





**SOLID ELECTROLYTE
INTERFACE (SEI)**
lithium ion covered with
electrolyte solvent reacts
with graphite

TEMPERATURE RISE FROM OUTSIDE/INSIDE

- Speeds up chemical reactions
- Electrolyte breakdown products formed on anode
- Lesser lithium ions nestled in graphite structure - lesser capacity





INTRODUCTION



- Achieving this goal requires breakthroughs in several areas - development of novel stable cathode & anode Materials, new electrolytes, additives that suppress side reactions
- A cheaper, viable & increasingly trending option is

SURFACE ENGINEERING OF THE
CATHODE- ELECTROLYTE INTERFACE

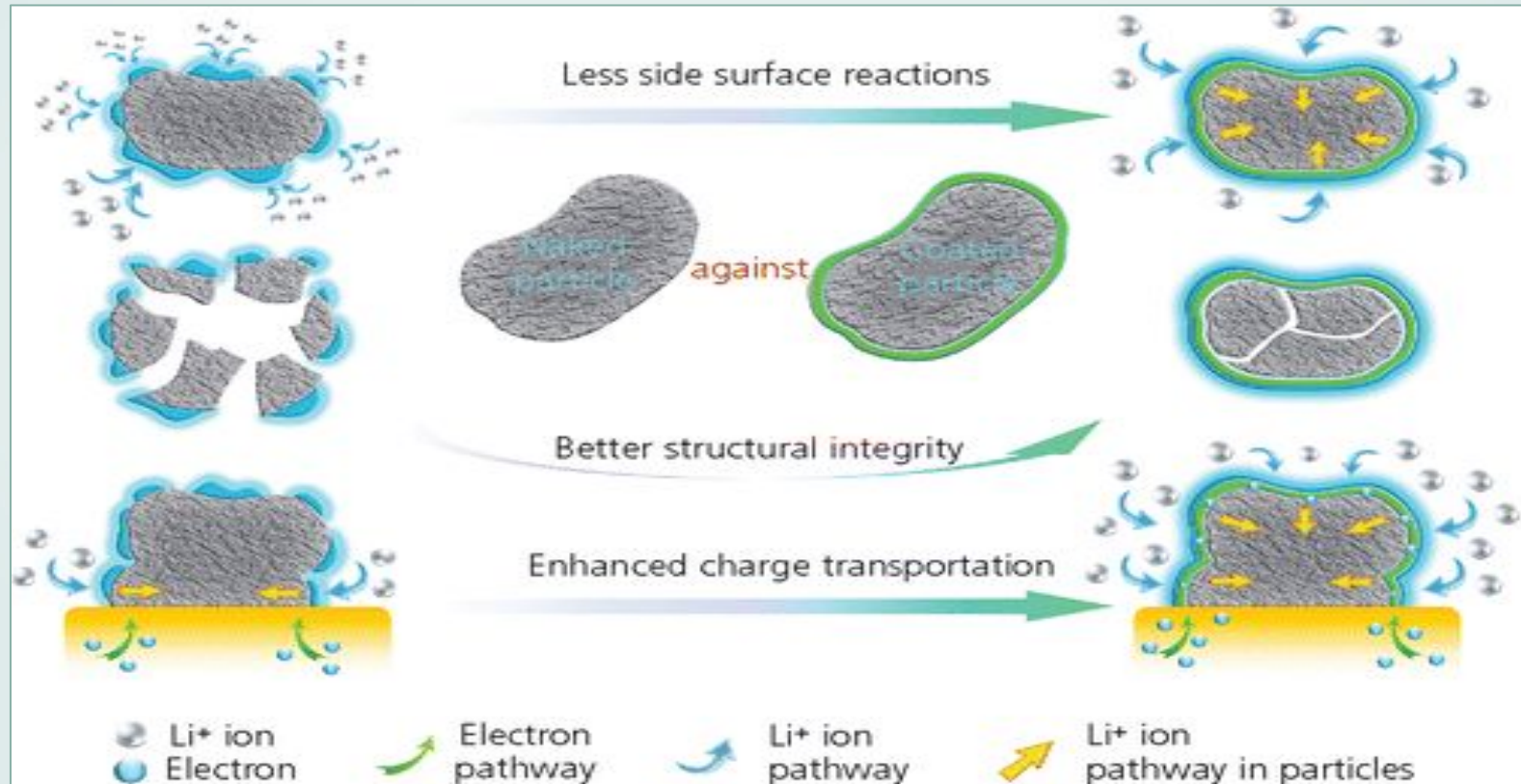


WHY SURFACE?



- The surface chemistry at the cathode–electrolyte interface is major factor responsible for the degradation of LIBs
- Charged electrode materials (delithiated cathode/ lithiated anode) tend to react with the non-aqueous electrolyte violently at elevated temperatures. These energetically favored side reactions can also occur slowly at ambient temperature, resulting in slow degradation of electrode materials
- An effective way to slow down the rate of these side reactions is to create an artificial physical barrier that raises their activation energy, resulting in a lower rate constant for ambient temperatures

For these, the engineering of the surface (metal-electrolyte interface) by various coating technologies is the most effective strategy to obtain desirable characteristics.



THE APPROACH

Solution offered & its
results





UNDERSTANDING SIDE REACTIONS



- Etching of the cathode material to release transition metals (TMs), whose deposition on anode will result in increased impedance for charge transfer
- TMs in cathode at their higher valence state upon charge are also labile against the organic electrolyte. can catalyze the oxidation of electrolyte, leading to formation of SEI and also releasing gases such as CO₂ and CO
- Cathode materials themselves are susceptible for structural degradation due to the unfavorable migration of TMs. In this way, the cathode surface experiences phase transition to lose its original structure, which is detrimental to the charge transfer & its stability during operation
- HF Scavenging When LiPF₆ decomposes in the presence of moisture, HF is one of the products, and it causes dissolution of the transition metals and surface corrosion of cathode materials.

THE MATERIAL

ELECTRO CHEMICALLY INERT

Extraordinary chemical and electrochemical stability displayed, especially at high voltages

Metal oxides & phosphates such as Al_2O_3 and AlPO_4 have been found to be improving LCO's performance

01

02

E- INSULATION, ION CONDUCTION

To reduce SEI layer formation. Lithium carbonate (Li_2CO_3) is an excellent option

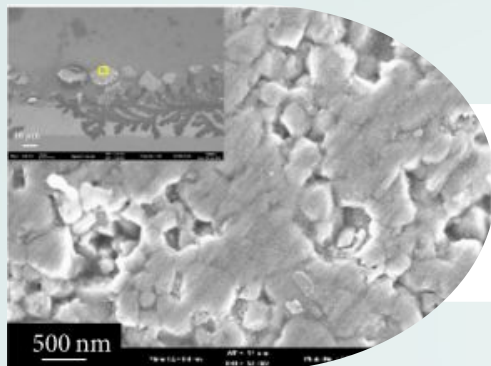
03

CAPACITY & DISCHARGE

Enhanced electrical conductivity, electrochemical performance shown which increases capacity
Achieved by Doping with Ni^{2+} , Mn^{4+} ions

Mn doped electrodes showing stable structure with much less structural changes during cycling

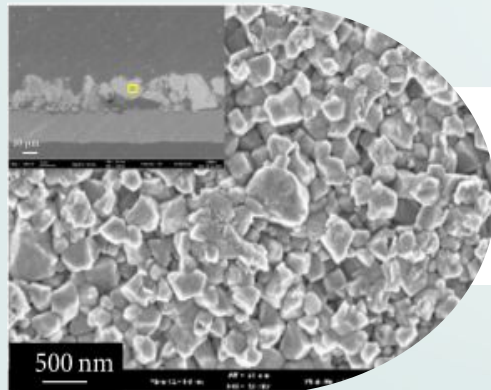
Enlarged cross sectional FE- SEM images



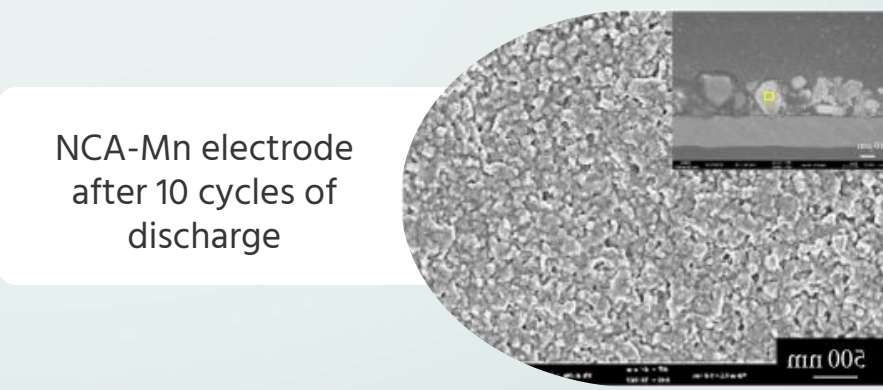
Fresh electrode of
NCA



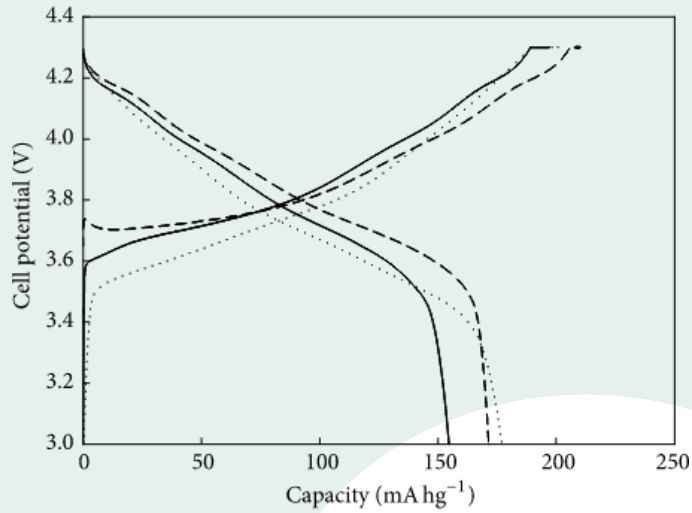
Fresh electrode of
NCA-Mn



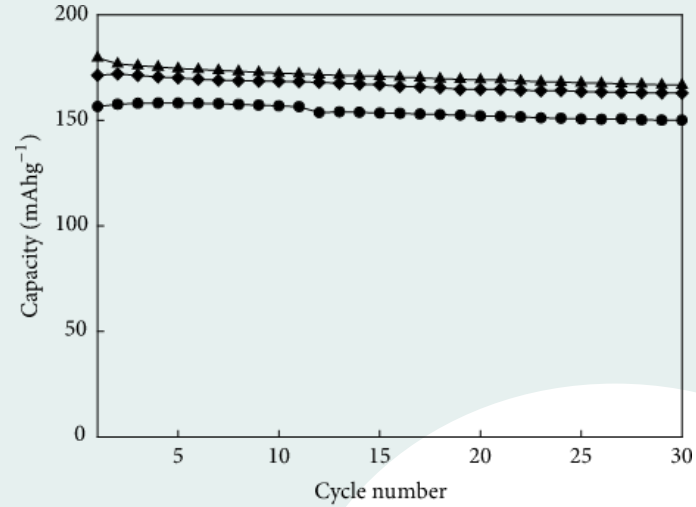
NCA electrode after
10 cycles of
discharge



NCA-Mn electrode
after 10 cycles of
discharge



Charge-discharge
profiles at first cycle of
pure electrode &
doped electrodes



Cycling performance
of NCA, NCA-Mn, and
NCA-Ti electrodes in a
voltage range of 3.0 to
4.3 V at 0.1C



COATING TECHNIQUES

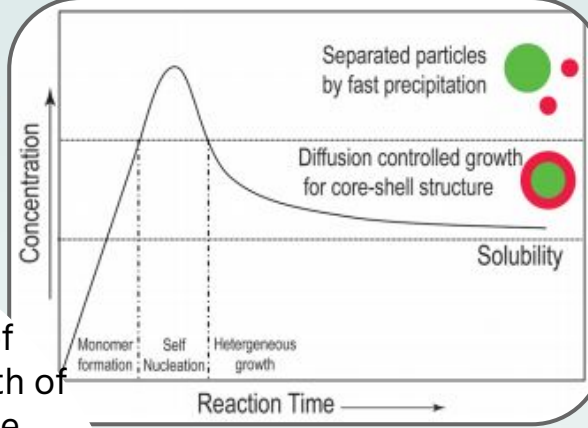


- For protecting effect, a complete coverage of the surface by the inert coating layer is more favorable. Therefore, it has been a continuous pursuit to develop simple & effective synthetic tools to achieve a robust, complete, and uniform surface coating
- Coating species like metal oxides/ phosphates, are not good for charge transfer, hence, need to be restricted to optimum thickness striking balance between stability & rate capability
- To achieve a uniform and conformal coating around the particles of different materials, a large variety of synthetic tools have been developed, which falls into two categories - wet-chemistry techniques or instrumental-based ones

WET CHEMISTRY ROUTE

For successful coating of selected species, the growth of the materials needs to be precisely controlled so as to wrap up the cathode materials instead of self-precipitating into separated particles, eventually forming a core-shell type structure with cathode material particles as the core

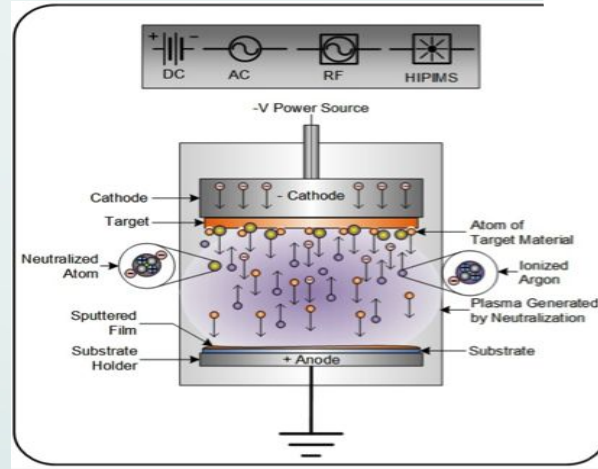
Growth control by -
Buffer solution
Slow releasing precipitant
Catalysis assistance
Charge interaction



INSTRUMENTAL BASED

Instrument based techniques have also provided powerful tools to build surface layers, which include Physical & chemical vapour depositions. ALD is one such CVD process while sputtering technologies like the follows are also used

RF sputter deposition
Magnetron sputtering





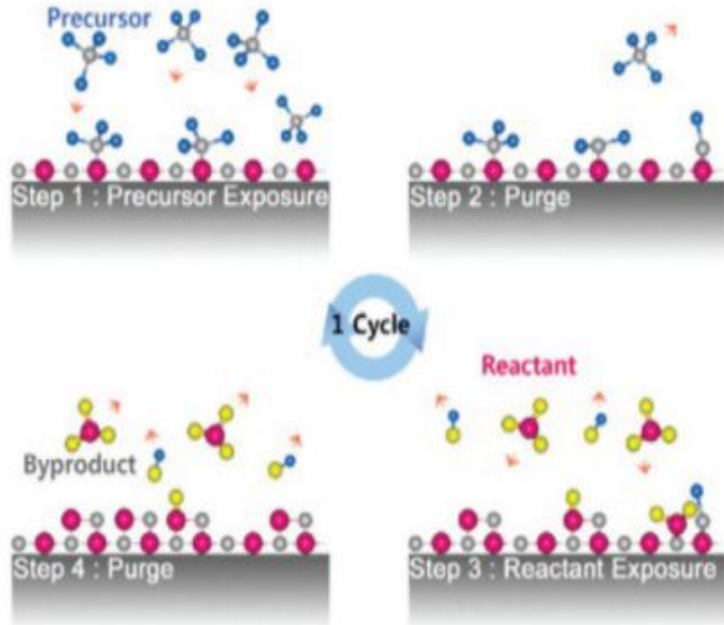
ATOMIC LAYER DEPOSITION



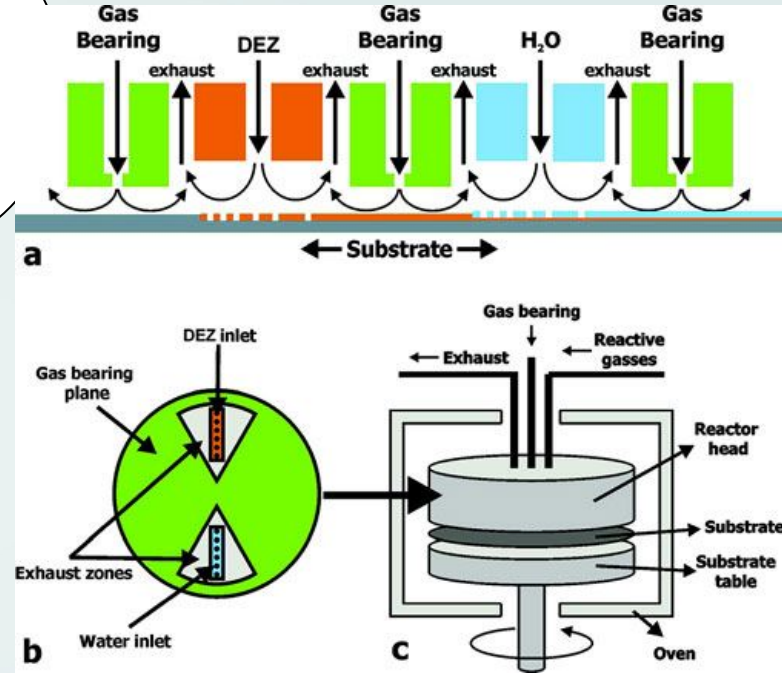
The ALD process based on binary reaction includes four steps:

- 1) A supply of precursor (e.g., $\text{Al}(\text{CH}_3)_3$) to trigger surface reaction with the reactive sites on the substrate (e.g. LCO particles), thus forming the intermediate and byproducts (CH_4)
- 2) A purging process using inert gas to evacuate the residual precursor and byproducts
- 3) A supply of reactant (H_2O) to react with the intermediate and generate the product (an AlOH^* layer) and new reaction sites (AlOH^*)
- 4) Repeated purging process to eliminate the excessive reactant and corresponding byproducts (H_2O and CH_4)

SCHEMATIC OF ATOMIC LAYER DEPOSITION



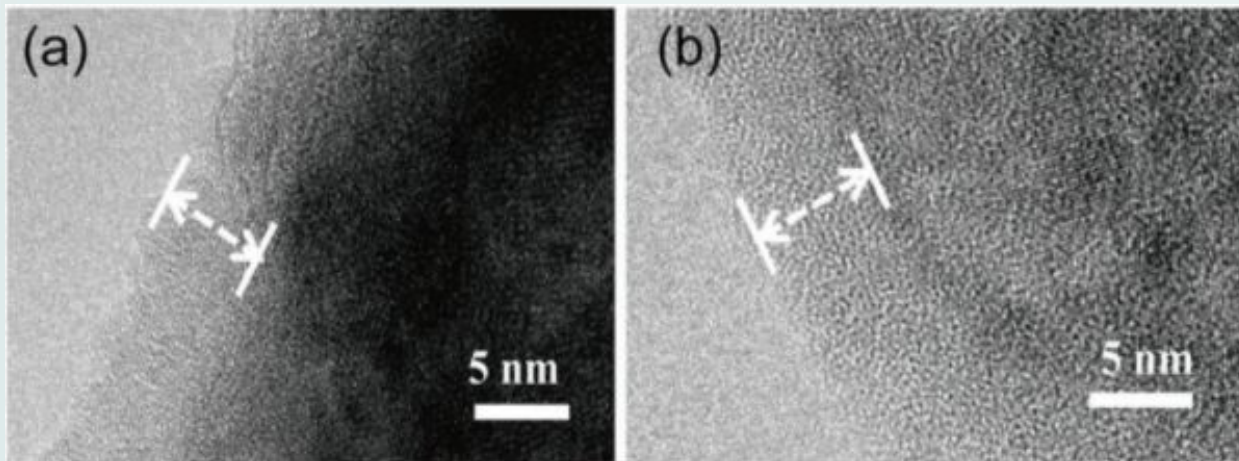
GROWTH PROCESS OF ATOMIC LAYER DEPOSITION



For each ALD cycle, a thin layer of the desired species is formed due to the self-limitation of the surface reaction, endowing the ALD technique a unique capability to form nanoshell with atomic layer accuracy.

Inspired by the extraordinary capability in surface control, ALD is being applied to different cathode materials to have a systematic investigation on the coating effect of high-energy materials

The performance of LCO cathode has been studied to demonstrate the effectiveness of the method

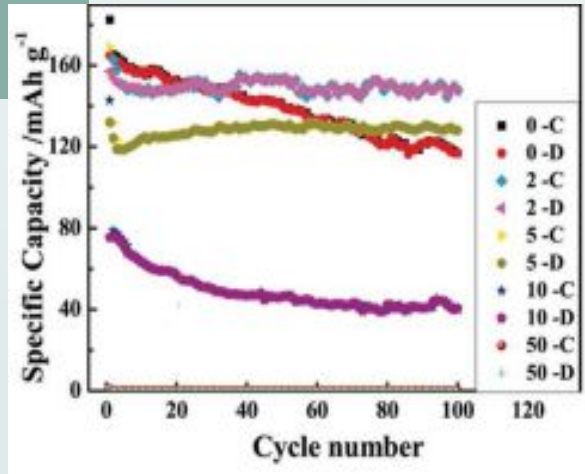


**HRTEM images of the LiCoO₂ cathodes by 50-ALD-cycles coating layers
a) TiO₂ and b) Al₂O₃.**

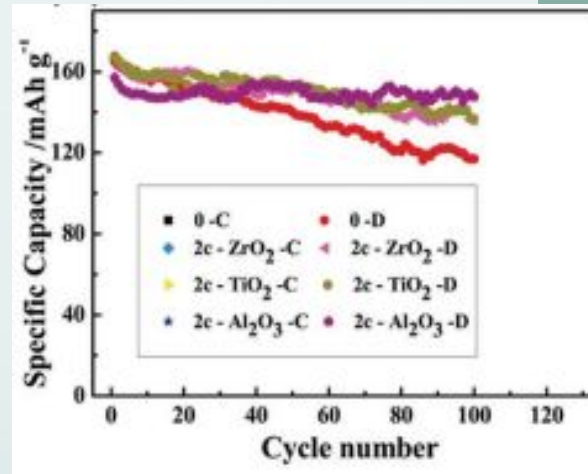
LCO cathode with 2 ALD cycles for Al_2O_3 coating showed the best cycling stability, which indicates that LCO with an ultrathin Al_2O_3 coating is able to improve its cyclability even at a high cutoff voltage

For comparison, a much thicker coating produced by extended ALD cycles(10) harmed the battery capacity.
This is due to resistance to charge transfer

Reversible charge
discharge capacity
 Al_2O_3 coated LCO
Different ALD cycles



Reversible charge discharge
capacity for 2 ALD cycles
coated LCO Different
metal oxide coats



An abstract graphic design on the left side of the slide. It features several organic, teardrop-like shapes in orange, olive green, and dark grey. A central dark grey shape contains a white circle with the number '03' in white. Other shapes include an orange one with a light green circle, a white one with a blue-green circle, and a dark grey one with a teal circle. There are also small solid circles in orange, white, and teal scattered around.

03

INFERENCE

Concluding remarks &
future scope

01

Working of an LIB
Shortcomings -
Formation of SEI,
Temperature
catalysing reactions

Why Surface engine-
ering necessary over
material research, Side
reactions influencing
coating

02

03

Desirable
characteristics of
coating material,
options available.
Strategies for coating -
Wet chemistry/
instrument based

Detailed study about
atomic layer
deposition
(instrument based
technique). Obtained
great results to satisfy
the objective

04



DRAWBACKS



- The trade off between rate capability & stability / energy density with the coating material used.
- The process isn't an ideal one - enormously time consuming - preparation of a pure substrate (effects the quality of finish), reaction time, challenges with concentrated coating (masking)
- Experiments have been performed mostly on LCO, LNMO cathodes which are stable in water & aqueous solution can act as a growth media for their surface control. However nickel rich cathodes are moisture sensitive & need development of reaction media which are harmless
- Typical ALD systems cost more than \$ 100,000. Which doesn't justify its use to improve LIB's performance by few more cycles.

POTENTIAL DEVELOPMENTS

ADVANCE COAT MATERIAL

Besides simple metal oxides, ALD could also prepare coatings of complex materials- ternary species, metal phosphates and fluorides with high conformity & precision

SURFACE DOPING

Instrument based doping techniques for bulk manufacturing. Increased depth of doping in a controlled way. Integration of chemical - mechanical processes

01

02

LOW COST ALD

Disintegration of equipment for individual processes. Build of separate reactors for precursor addition, purging

03

EXHAUSTIVE STUDY

Cutting edge surface sensitive characterization techniques (HRTEM), ab initio calculations, molecular dynamics need to be adopted to investigate the impact of ALD coating on the kinetics of charge transfer and mass transfer through the surface of cathode materials

04



OTHER POSSIBILITIES



- While ALD is an amazing technique, other PVD, CVD techniques could also be looked at slight loss of precision but an economically better solution. RF Sputter deposition is one such technique.
- In situ growth & carbonization is another process through which surface doping is achieved. Substrate is dispersed in a solution and source is dissolved by magnetic stirring. Advance materials such as Zeolitic imidazolate frameworks-8 (ZIF-8) (is a class of porous materials) could be used with this technique.
- A study was performed using the CASTEP program from Accelrys, Inc. An ultrasoft pseudopotential density functional theory (DFT) method was used to see how nitrogen could be doped on surface of diamond during its growth using CVD. Similarly Ni and Mn ions could be doped to develop surface doping



REFERENCES



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- [3] Effect of CVD diamond growth by doping with nitrogen - <https://link.springer.com/article/10.1007/s00214-013-1432-y>
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- [5] Effect of Metal (Mn, Ti) Doping on NCA Cathode Materials for Lithium Ion Batteries - <https://www.hindawi.com/journals/jnm/2018/8082502/>
- [6] Role of surface coating on cathode materials for lithium ion batteries
- [7] Protective Spinel Coating for $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Mn}_{0.50}\text{Co}_{0.17}\text{O}_2$ Cathode for Li-Ion Batteries through Single-Source Precursor Approach - MDPI
- [8] Learn Engineering <https://www.youtube.com/channel>



PRESENTATION SESSION

QUERIES & SOLUTIONS



AJAY KUSHWAHA'S QUESTION : *If metal oxides resist charge transfer, why are they being used as coating material ?*

Metal oxide would certainly resist charge transfer and is not ideally the best coating material. But it stabilizes the cathode to a great extent and resists any microstructural changes. This in turn decreases the rate of degradation of capacity.

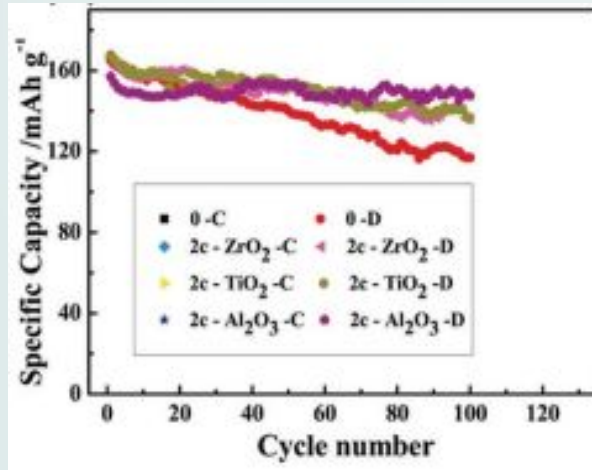
So, the key is the optimum thickness of the layer. If the layer is more than 10 nm in size, the charge transfer resistance could be problematic if it's very less (< 4 nm) then it serves no purpose. Hence the correct size is important here.

Also, as mentioned in the future scope, newer materials that can be coated by using ALD / chemical methods are also being tried out

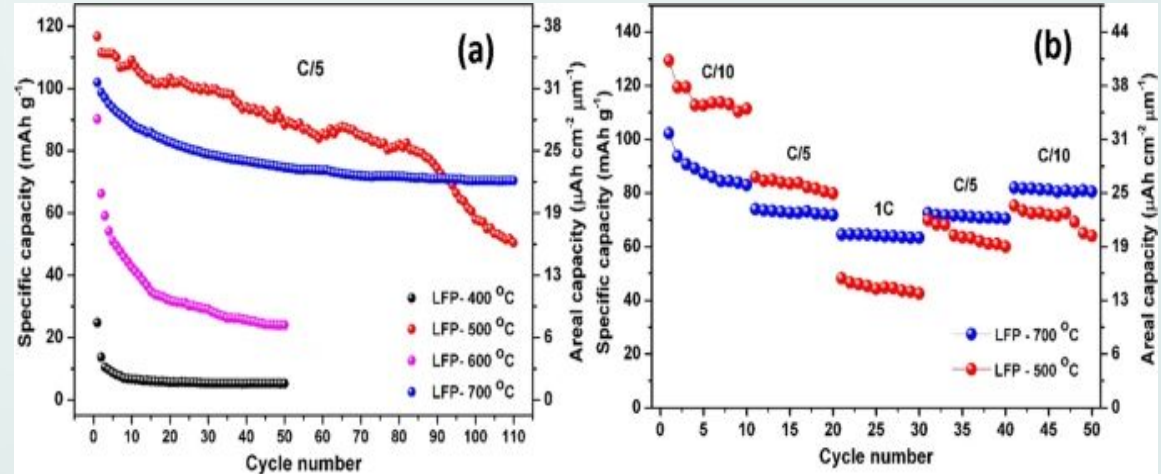
PROJECT GUIDE'S QUERY & SCOPE FOR IMPROVEMENT

Why only ALD when it clearly has many drawbacks? Show how it is better than other methods like PVD?

ALD coating on LCO cathode



PVD coating on LFP cathode



Though a clear comparison couldn't be made due to lack of literature in PVD methods being used for coating of cathodes in LIBs, it can be observed that they couldn't deliver the performance that ALD technique could achieve.

This is mainly due to the precision & accuracy in nano meter that ALD promises. Also the reactant holds on to the substrate better due to the surface chemical reactions in ALD. on the other hand, ions are just sputtered in PVD hence high stability of the interface is not guaranteed after certain number of cycles. Hence, the rate of decrease of capacity is high in PVD coated electrodes

Though ALD is costly, the best PVD techniques that can offer more precision are much costlier than ALD, hence eliminating its use

Other methods like chemical, though promise outstanding results aren't being preferred due to the absence of equipment/ setup based manufacturing which is key for large scale production



THANK YOU!