

| REPORT DOCUMENTATION PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                  |                                                      |                               |                                             | Form Approved<br>OMB No. 0704-0188        |  |
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| 14. ABSTRACT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                  |                                                      |                               |                                             |                                           |  |
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U.S. Army Research, Development and Engineering Command

# Ionic Additives for Electrochemical Devices Using Intercalation Electrodes



***TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.***

**Inventor: Dr. Kang Xu**

ARL 09-18

APPROVED FOR PUBLIC RELEASE

February 16, 2011

This invention relates to an ionic additive technology that modifies the edge sites of a graphitic anode to ease  $\text{Li}^+$  (lithium ion) transport. The invention greatly reduces power-robbing effects of “charge transfer” resistance.

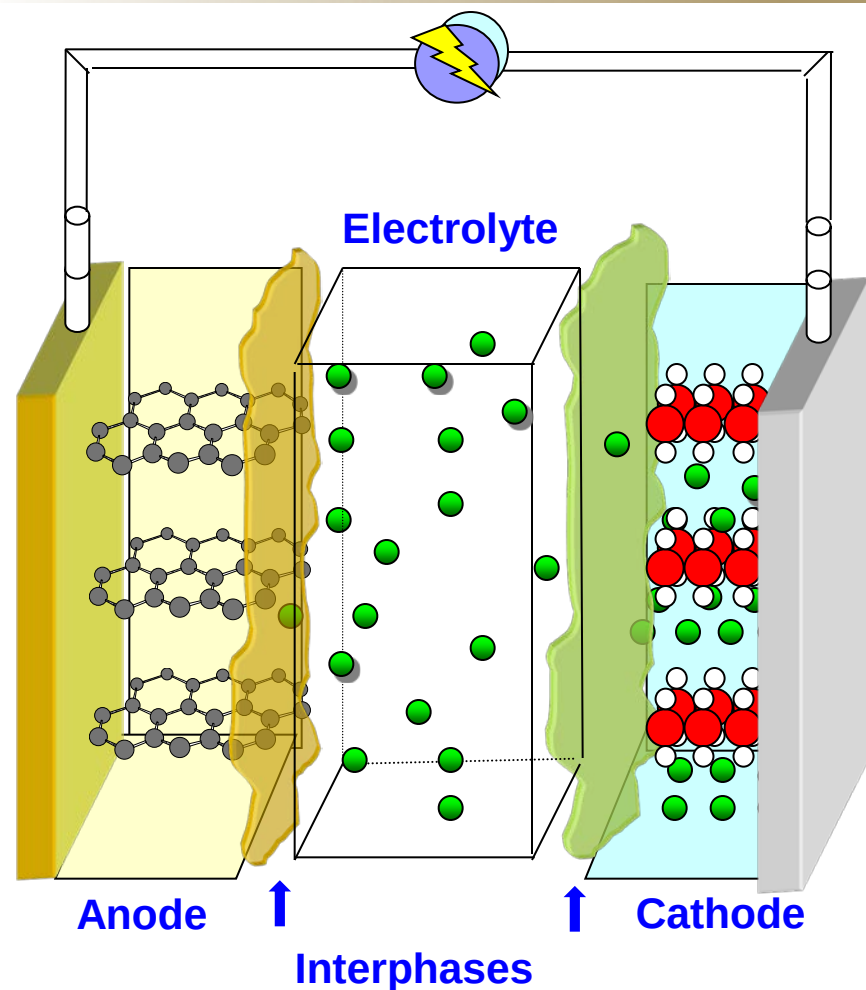
## How Li Ion Battery works

- Li ion battery is an “intercalation” battery chemistry
- Graphite is the “universal” anode used in Li ion batteries
- $\text{Li}^+$  transport at graphite constitutes the most difficult step and it dictates the power density of a Li-ion device

## The new ionic additives form a new interphase that facilitates $\text{Li}^+$ transport

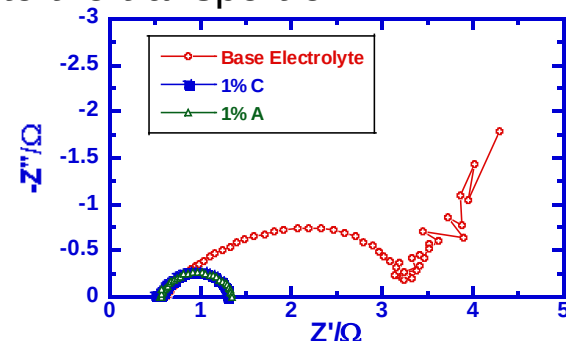
- Reduces “charge-transfer” resistance by 2/3
- Activation energy barrier lowered to ~40 kJ/mol vs. current 60~70 kJ/mol
- Faster  $\text{Li}^+$  movement = Higher Power Density

The additive material is easily available from commercial source, is low cost and has minimal impact on the existing battery manufacturing processes

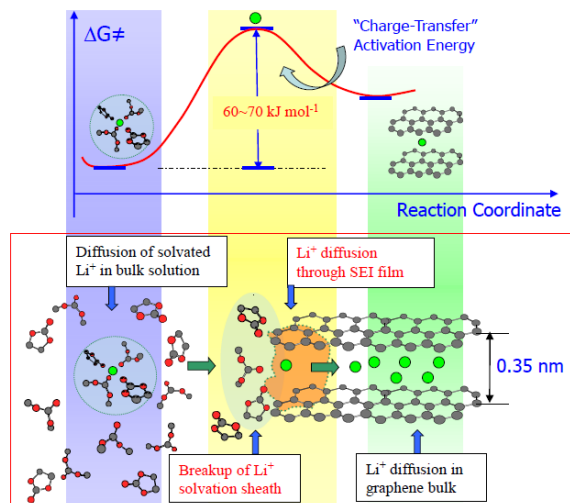
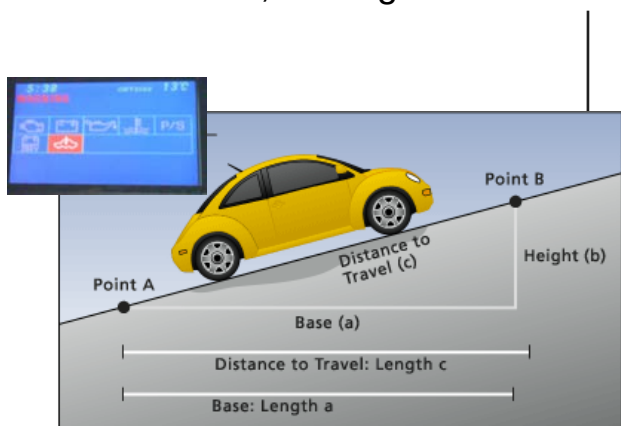


The innovation is part of a family of ionic additive compounds based on a salt with a cation (positive ion) that can be reduced into metal at  $> 1.0$  V at intercalation sites. The result is graphite edge sites with “metallic” nature that are more receptive to the transport of  $\text{Li}^+$ .

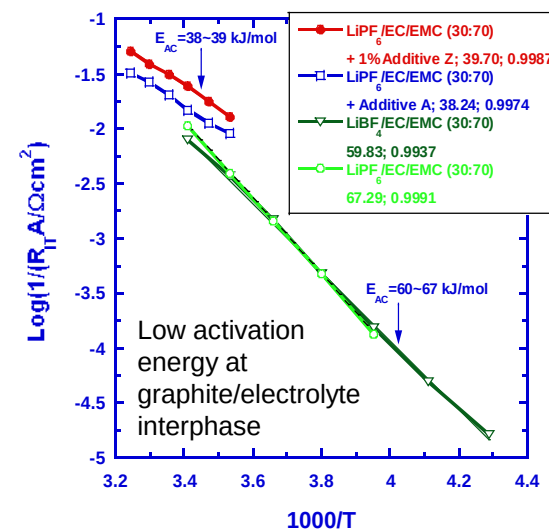
- Current electrolyte usually results in  $\sim 60\text{--}70$  kJ/mol energy barrier and  $> 3 \Omega$  resistance at graphite/electrolyte interphase in a  $0.97 \text{ cm}^2$  electrode
- $< 1\%$  additive of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  salt dramatically improved both interphasial resistance ( $< 1.5 \text{ W}$ ) and activation energy barrier ( $< 40$  kJ/mol)
- The metal clusters precisely targets the edge sites of intercalation electrode, leaving



Activation energy barrier at graphite/electrolyte interphase



Low impedance at graphite/electrolyte interphase



Low activation energy at graphite/electrolyte interphase

## Challenges addressed by the invention:

- Graphite is the “universal” anode most Li ion batteries
- However, the electrolyte/graphite interface is very resistive
- Previous attempts to address this resistive interface (e.g. metal coating) are difficult, expensive and “indiscriminate”

These additives in this invention pave a very simple but effective path for surface modification of graphite or any other intercalation electrode

- Specifically targets the “edge-sites” :  $\text{Li}^+$  intercalation sites
- Achieves “nano-metallization” at the edge sites
- Effectively reduces the interphasial resistance
- Flexible and open system
  - Deposition potential of ionic additives tunable
  - Can be combined with the 5 V electrolyte technology

## Easy access and inexpensive method to prepare

- Precursor materials readily available from commercial source
- Simple mix with state-of-art electrolyte

Batteries used in electric vehicles (EVs), especially in hybrid power systems, require high power density

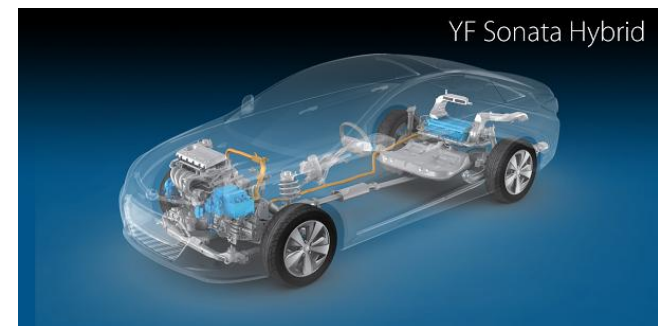
- to capture the regenerative energy only present during the 10 seconds scale
- To release the energy while accelerating

An ordinary graphite anode fails to rapidly capture such energy produced

- Slow  $\text{Li}^+$  transport at edge site interphase doesn't allow capture or release of the energy on the required time-scale because of high resistance
- High resistance also leads to metal Li deposition
  - Service life shortened
  - Potential hazard: fire and explosion

This invention provides an easy and simple solution for a high power density graphitic anode

- Open system: accommodates various cathode chemistries
- Increased service life and safety
- Can be combined with 5 V electrolyte additives







## Method of Preparation of Novel Additives

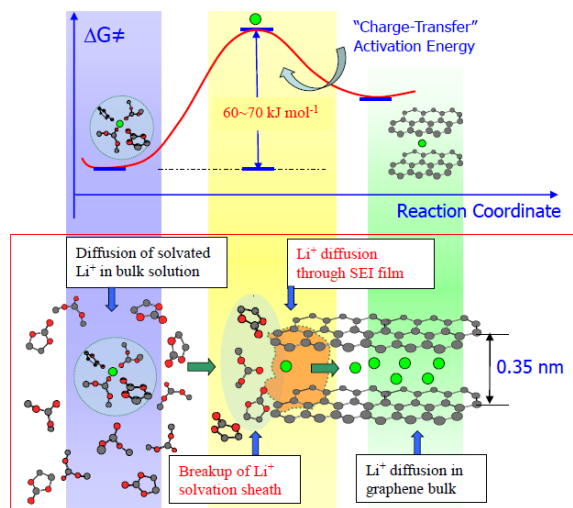


Simple electrolyte mixing  
in glovebox or dryroom



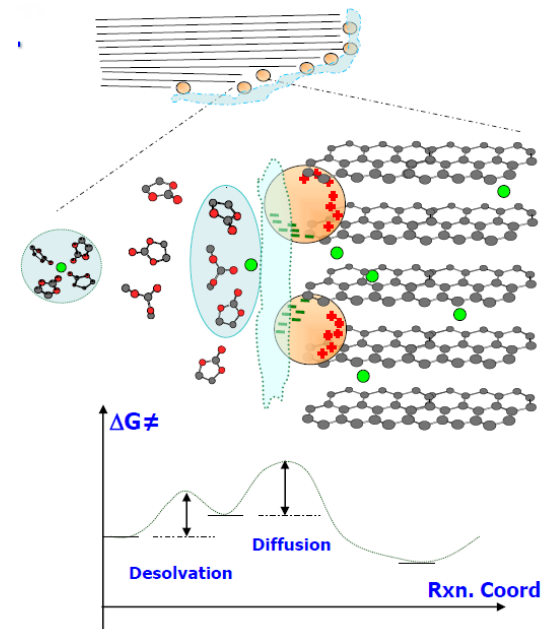
Coin cells assembled using  
industry standard electrodes

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Energy barrier of  $\text{Li}^+$ -transport across the interphase at edge-sites of an intercalation electrode

Ionic additive of the invention introduces “metallic” nature that assists  $\text{Li}^+$ -transport



TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Military applications would significantly benefit from the improvement in commercial Li ion technologies

- Major Impact: Military HEV operation and “silence surveillance “ capability
- Reduction of logistic burden
- High power applications: EM gun/EM armor/Directed Energy Weapons



APU in various Military Vehicles



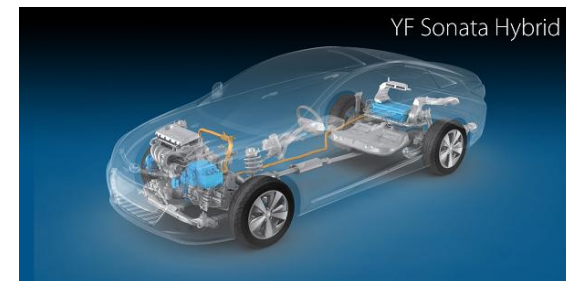
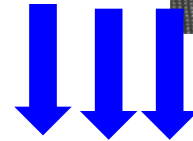
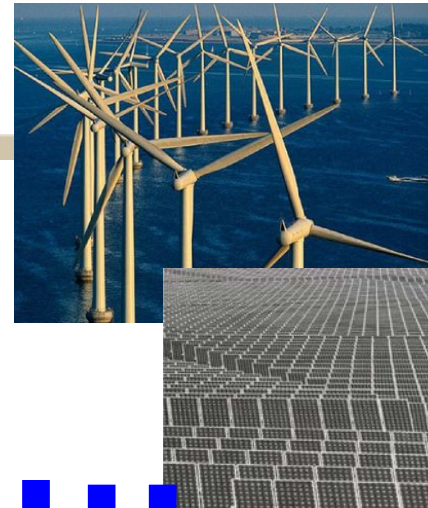


The invention can benefit a number of commercial battery applications, including

- Vehicle electrification applications (HEV/PHEV/BEV)
- Large-scale energy storage devices (grid-stabilization, load-levelling)

Additionally, the invention can benefit other applications that employ intercalation-type electrodes, including:

- Ultracapacitors
- Hybrid capacitors
  - The activated carbon could be modified to facilitate charge-accumulations at the electrolyte/electrode interfaces



A patent license and CRADA is sought.

- The current technology would benefit from a collaboration between the inventor team and the commercialization partner in order to speed the development to the market. This would most readily be done through a CRADA/patent license agreement. The inventor team is available to work with commercialization partner
- TRL 5 – Fully functioning battery prototypes using coin and pouch cell formats
- A patent application has been filed