Advanced Lithium-Ion Battery technologies for plug-in hybrid electric vehicles

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Outline

I- Introduction

II- Results

- *Electrochemical and thermal properties of the new electrolytes.*
- *Battery testing using the new electrolytes.*
- *Preparation and battery testing of nanoparticles of the high voltage $LiNi_{0.5}Mn_{1.5}O_4$ cathode material*

III- Conclusions

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Introduction: Requirements for a battery in HEV/PHEV.

- *High power density and energy density.*
- *An operating temperature range from -30 °C to +50 °C.*
- *Long calendar life similar to that of the vehicle.*
- *Safe: Abuse tolerant especially on Nail and Crush tests when battery components are exposed to air (less reactive anode).*
- *Cheap.*
- *Environmentally friendly.*

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Introduction: Advantages/Disadvantages of Li-ion batteries

Advantages :

- *High operating voltage ~3.7 V. (three times more than NiMH ~1.3 V).*
- *High specific and volumetric energy "120-160 Wh/Kg". (two times more than NiMH "60-75 Wh/Kg").*
- *Low self discharge (5% per month, over 30% per month NiMH)*
- *Good cycle life (still to be increased for PHEV applications)*
- *No memory effect.*

Disadvantages:

- *They utilize flammable, volatile, corrosive electrolytes.*
- *They are more expensive than other battery technologies.*

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Motivation

I- To replace conventional electrolytes (e.g. $LiPF_6$ in EC/DMC) by electrolytes that are:

- *Safer (use of "Adiponitrile'' a solvent with higher boiling point; higher flash point and higher autoignition temperature).*
- *Electrochemically more stable at high voltages.*

II- To produce nano high voltage cathode materials:

- *This would increase the energy/power density and rate capability of the battery and possibly its safety by rendering the use of $Li_4Ti_5O_{12}$ (safe anode) and retaining the high operating voltage of the batteries*

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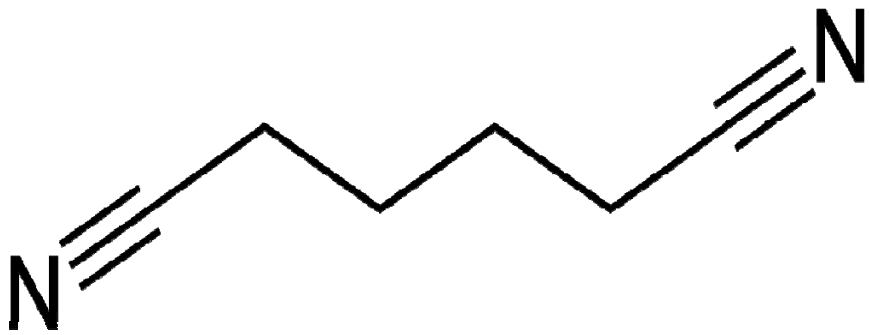
Adiponitrile, ADN, a thermally and electrochemically stable solvent

- *Has low volatility (B.p. ~ 300 °C)*
- *Has low flammability (F.p. >160 °C)*
- *Good solvating properties.*
- *Commercially available and relatively cheap.*



1,4-Dicyanobutane

	Mp	Bp	Fp	T_{ig}
DMC	2-4 °C	90 °C	18 °C	
DEC	-43°C	126°C	25°C	445°C
EC	34-37 °C	246.7 °C	160 °C	450°C
ADN	1 °C	295°C	160°C	550°C

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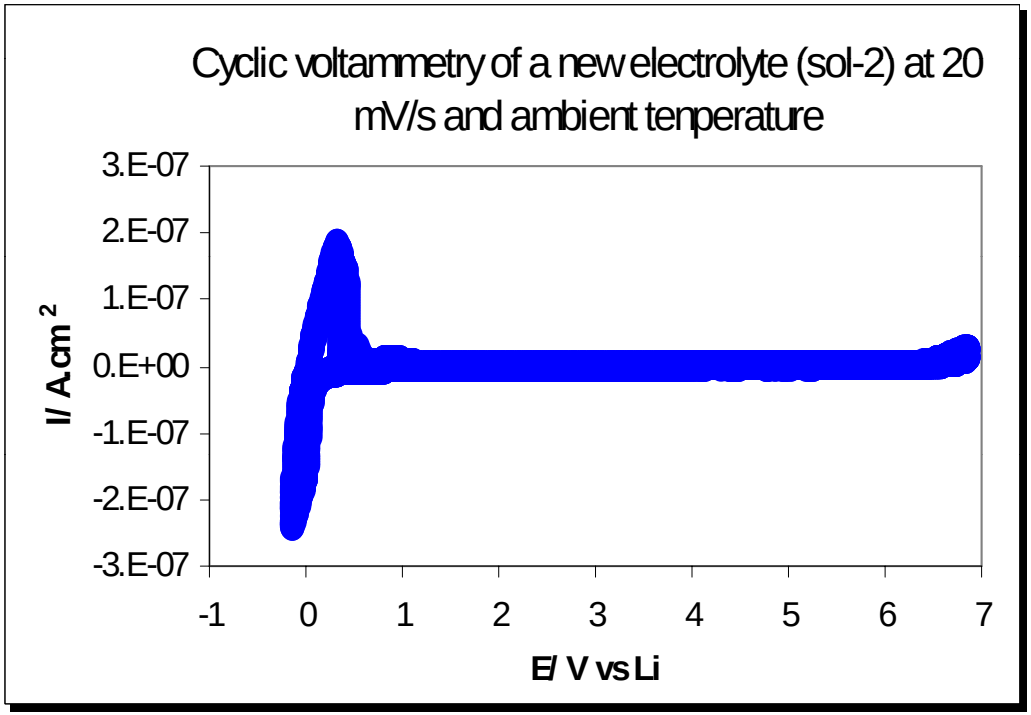
ADN electrolyte: cyclic voltammetry

- *The ADN electrolyte made by mixing with the non-corrosive LiTFSI salt (1M) shows a wide electrochemical window extending over 6.5 V.*
- *This is 1.5 volt higher than the commercial electrolyte*



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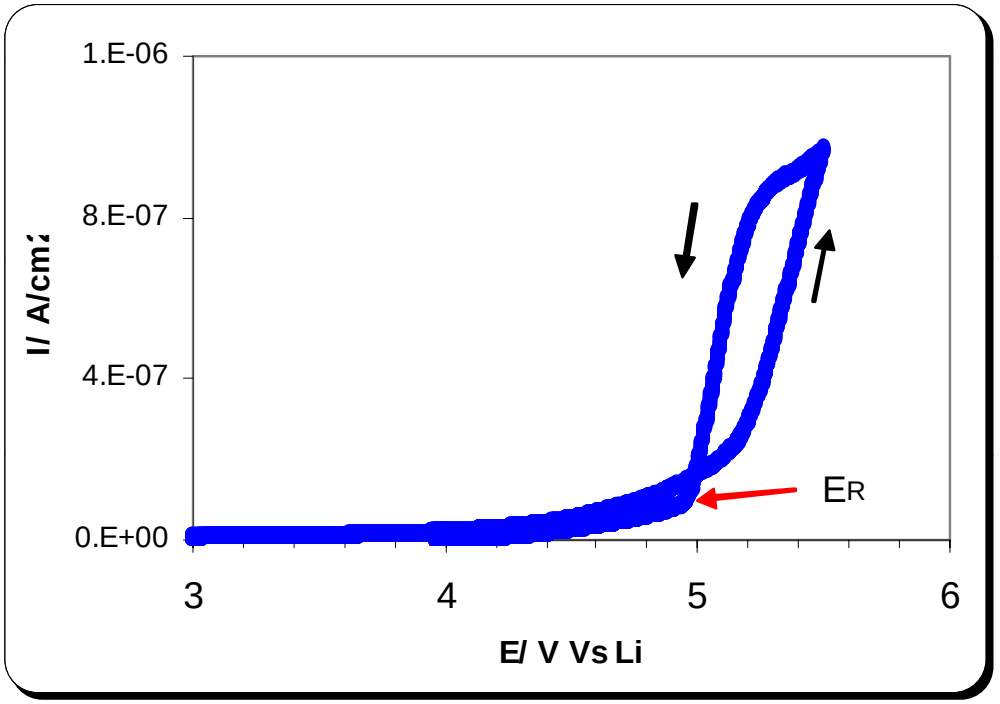
ADN electrolyte: Aluminum corrosion

- *Aluminum is the preferred current collector in Li-ion batteries because of its low cost and light weight .*
- *The ADN electrolyte shows a greater stability against aluminum with a re-passivation potential (E_R) value of 4.8 V.*
- *This is 1 volt higher than the commercial electrolyte*



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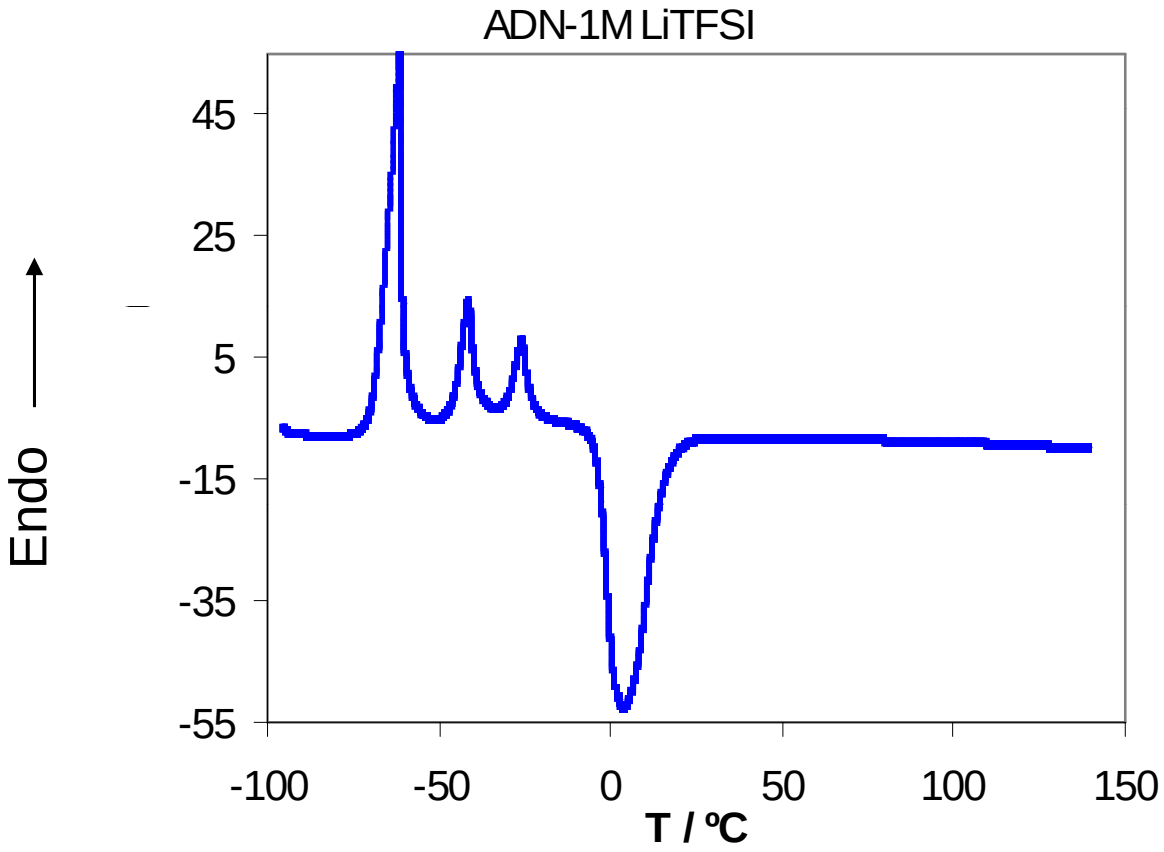
ADN electrolyte: DSC

- *The ADN electrolyte is more thermally stable than the commercially available 1 M $LiPF_6$ EC:DMC (45 °C).*
- *The electrolyte has a high melting point (5 °C).*



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ADN electrolyte: preliminary battery testing

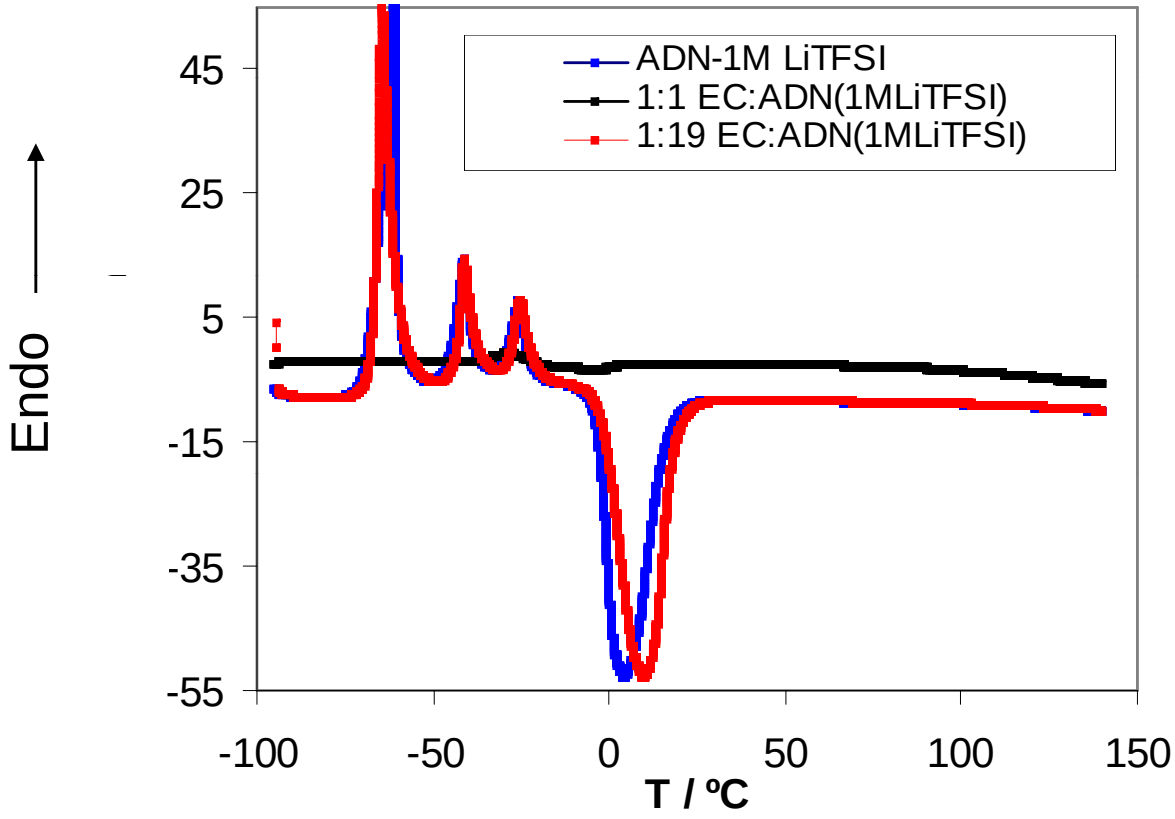
- *Initial battery testing showed that the ADN electrolyte does not work in a battery*

- *Explanation: ADN is not able to form a compact, conducting solid electrolyte interface, SEI.*

- *Solution: we need to add EC (ethylene carbonate, a good SEI former) as a co-solvent (1:1 v/v) or additive (1:19 v/v or 5 w.t.%)*

EC:ADN electrolytes: DSC

- *The 1:1 electrolyte is a miscible solution with a low melting point.*
- *The 1:19 still shows the 5 °C melting peak.*
- *The 1:1 and 1:19 electrolytes are more thermally stable than the commercially available 1 M $LiPF_6$ EC:DMC (45 °C).*



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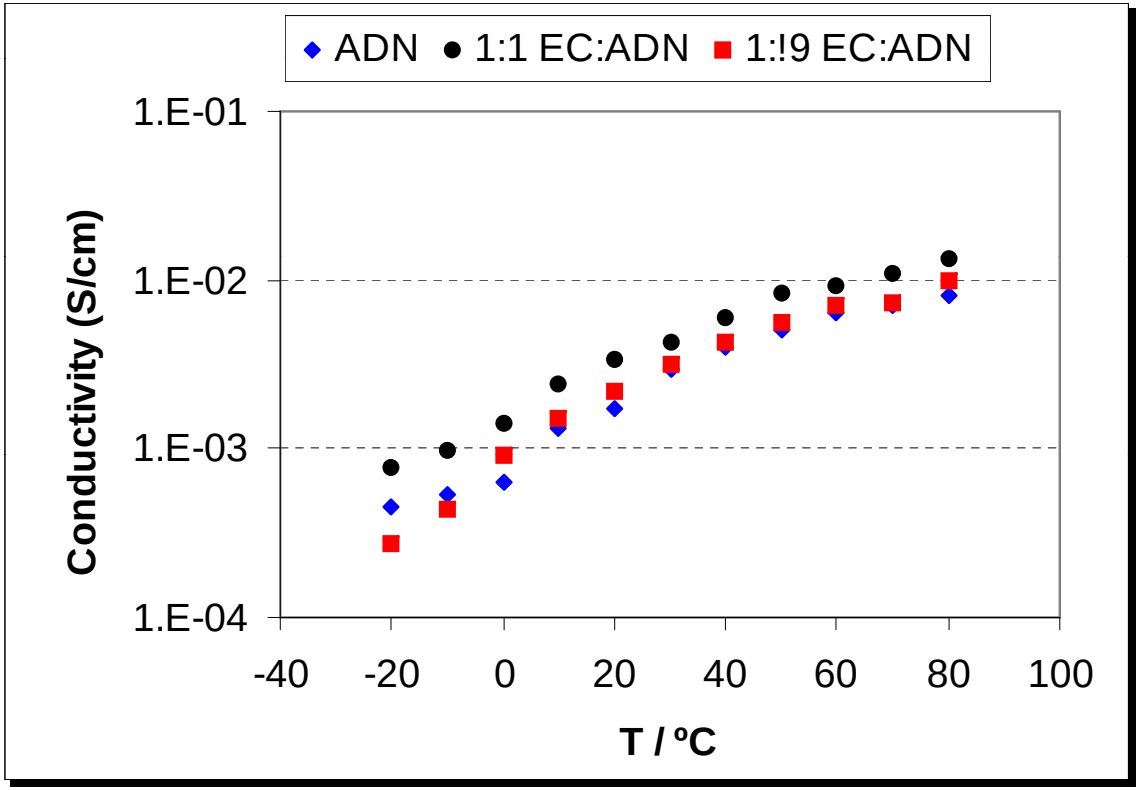
EC:ADN electrolytes: Conductivity

- *All the electrolytes showed good conductivities exceeding 1 mS/cm at 20 °C.*
- *The 1:1 And the 1:19 increased the conductivity of ADN reaching in the case of 1:1 to 3.4 mS/cm at 20 °C.*
- *LiBoB salt, a good SEI former, was found to have limited solubility in ADN (0.17 M) was added to the electrolyte (0.1 M).*



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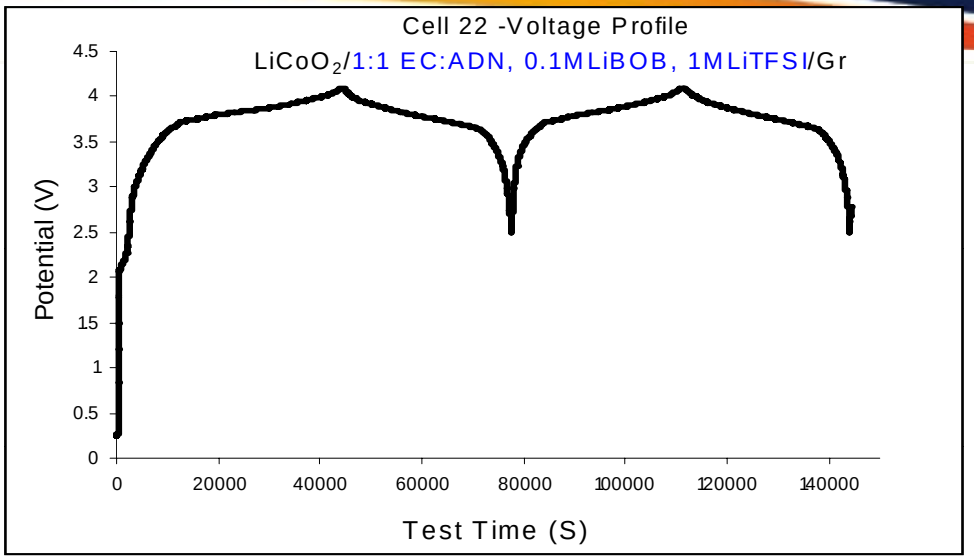
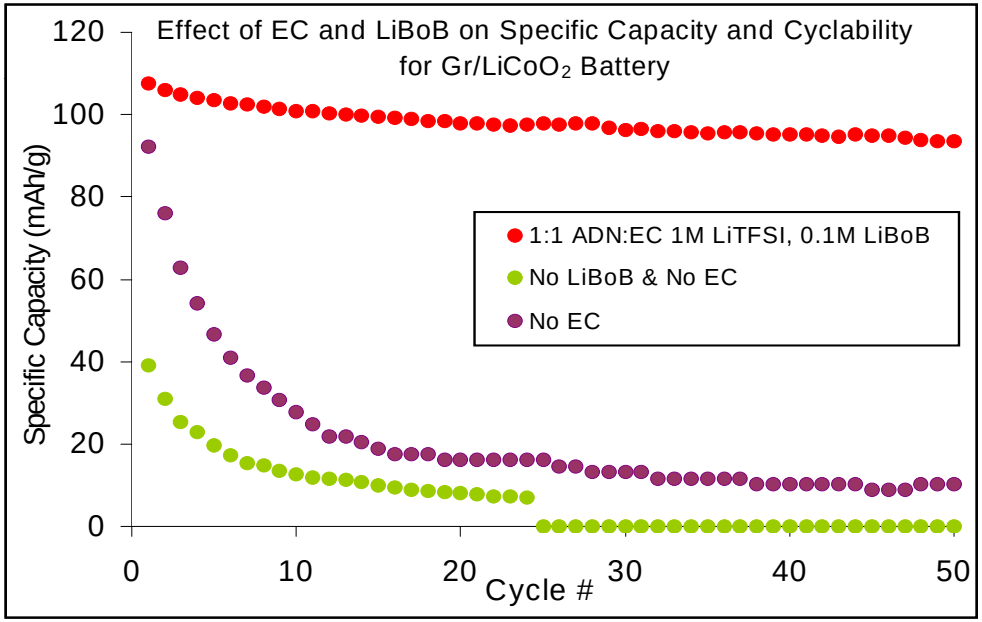
Battery performance: Electrolyte: EC:ADN (1:1) 1M LiTFSI + 0.1 M LiBoB; Electrodes: Graphite/$LiCoO_2$

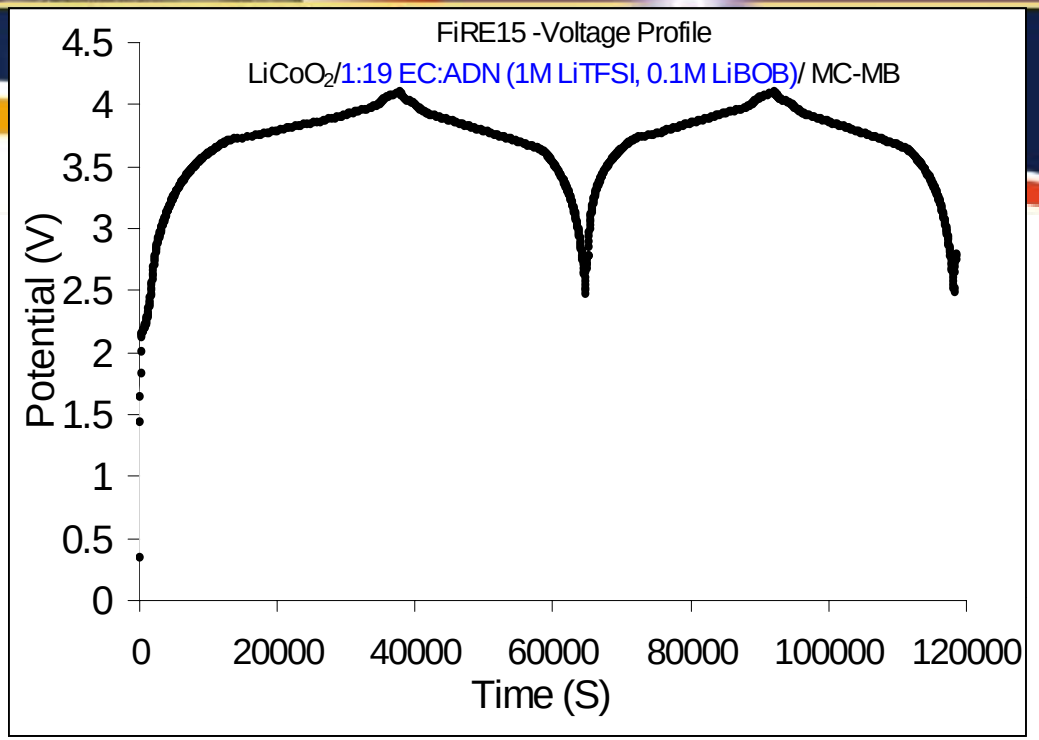
- *Batteries using ADN with no EC or LiBoB do not work.*
- *When EC is used along with LiBoB the battery gives good capacity.*
- *The 1:1 EC:ADN gives initial discharge capacity of 115 mAh/g with good retention up to the 50th cycle.*

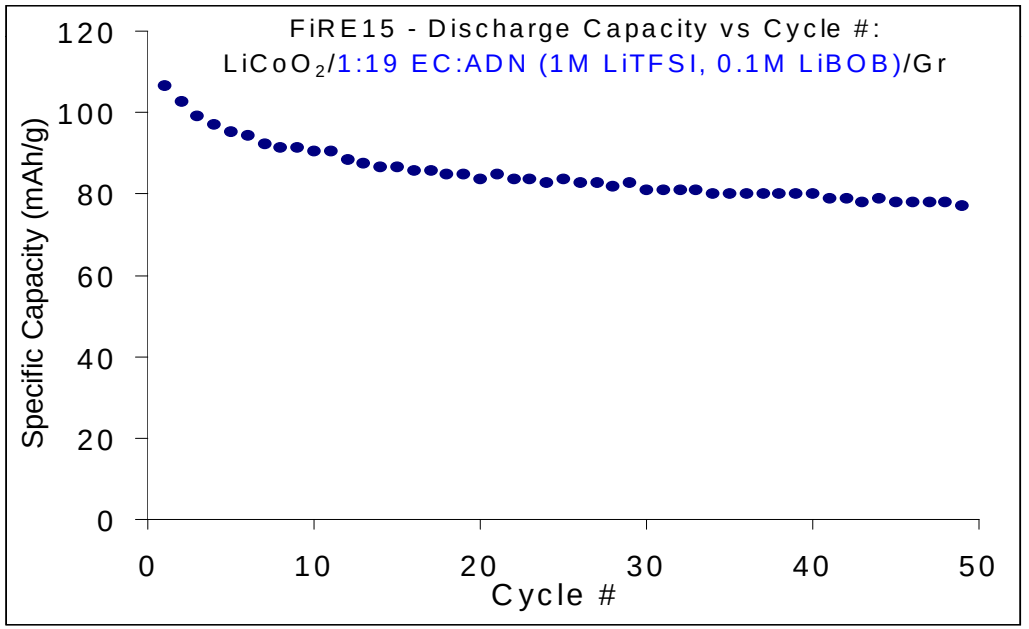




Battery performance: Electrolyte: EC:ADN (1:19) 1M LiTFSI + 0.1 M LiBoB; Electrodes: Graphite/$LiCoO_2$

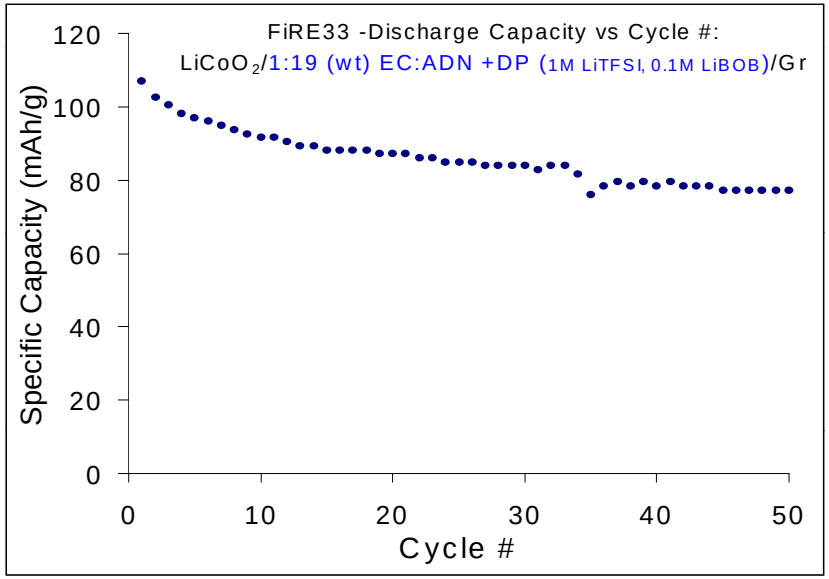
- *Initial discharge capacity of 110 mAh/g with little loss up to 50 cycles.*
- *Excellent coulombic efficiency.*

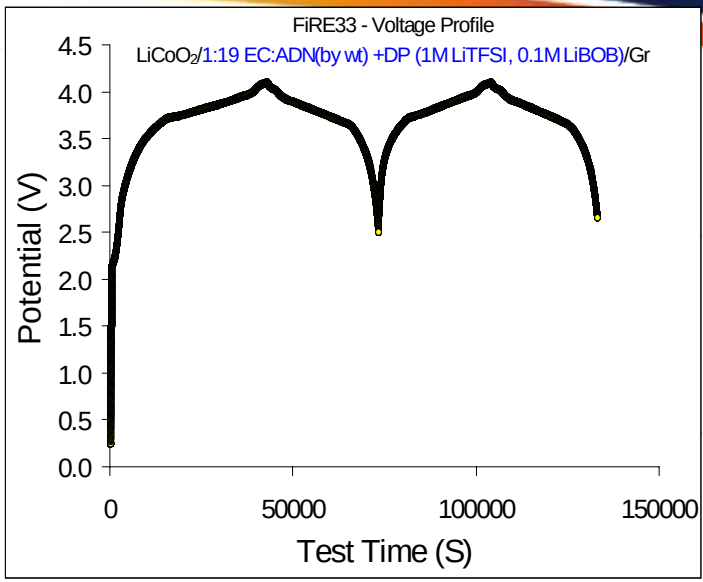


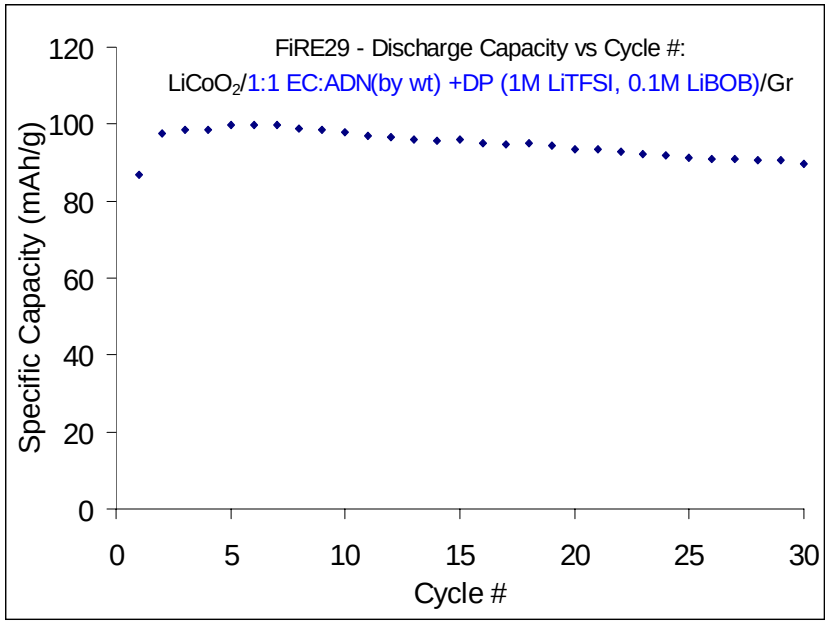


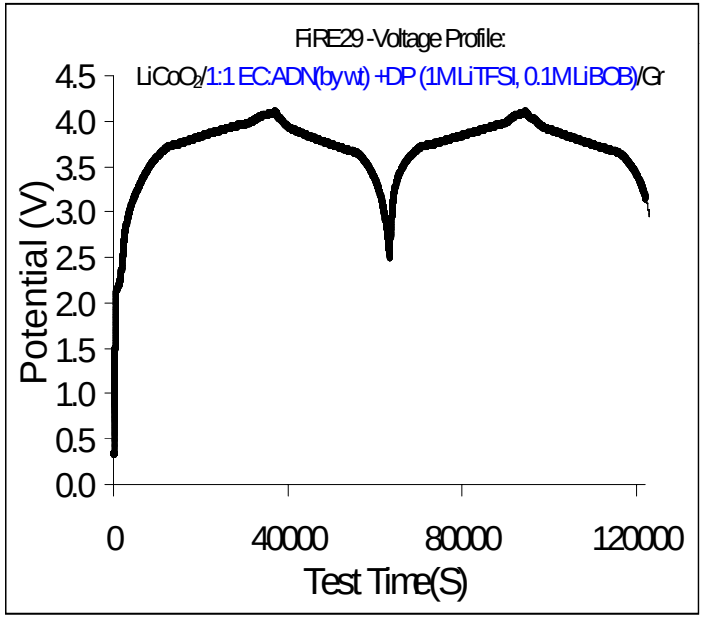
Battery performance: Effect of Diphenyl, DP, 2 w.t.% electrolyte additive : EC:ADN

- *DP shows no effect on the capacity of 1:19.*
- *DP improves the capacity and cyclability of the 1:1 electrolyte.*
- *Discharge capacity of 80 mAh/g for the 1:19 after the 50th cyclcle and 95 mAh/g for the 1:1 after the 30th*



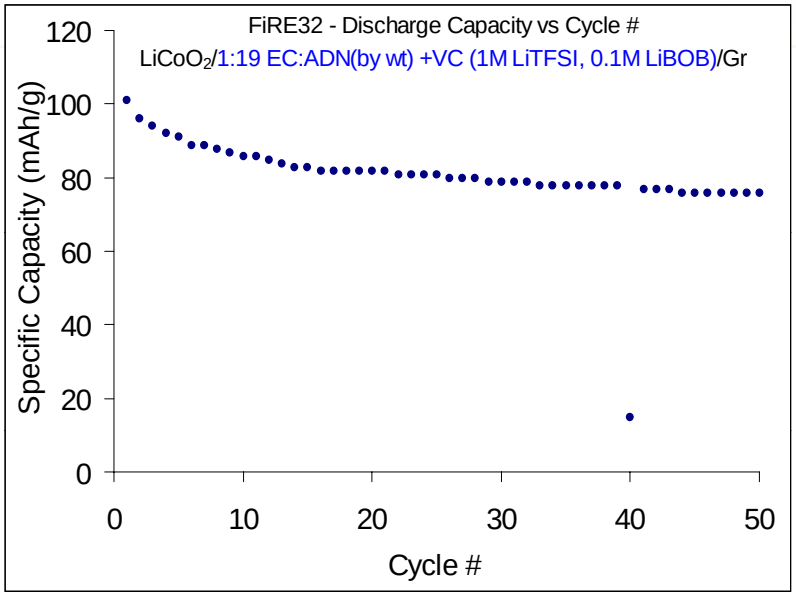


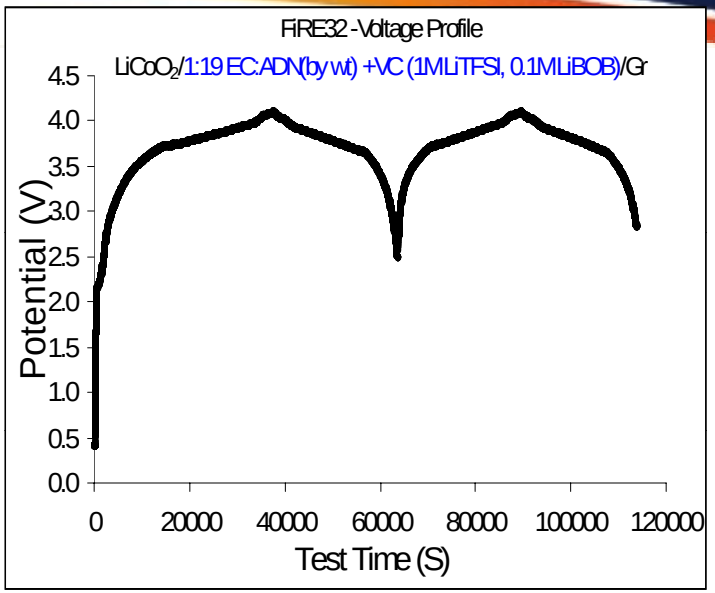


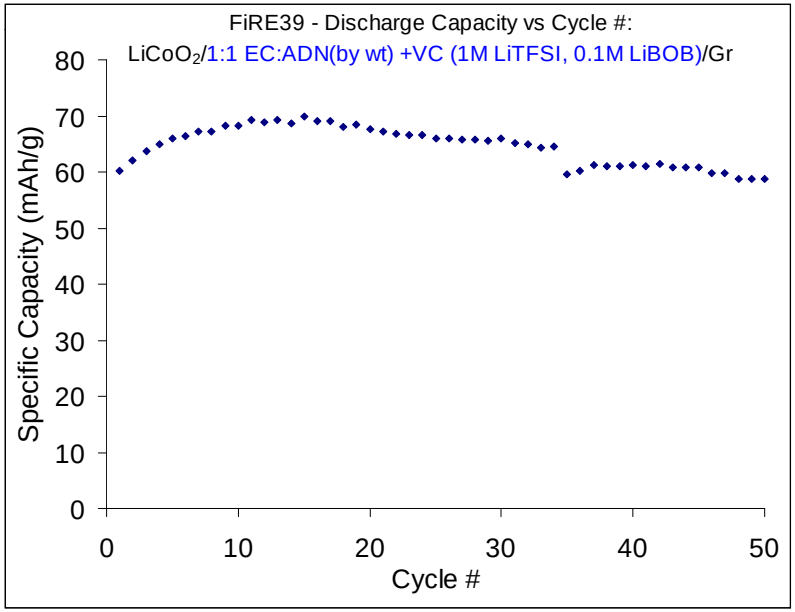


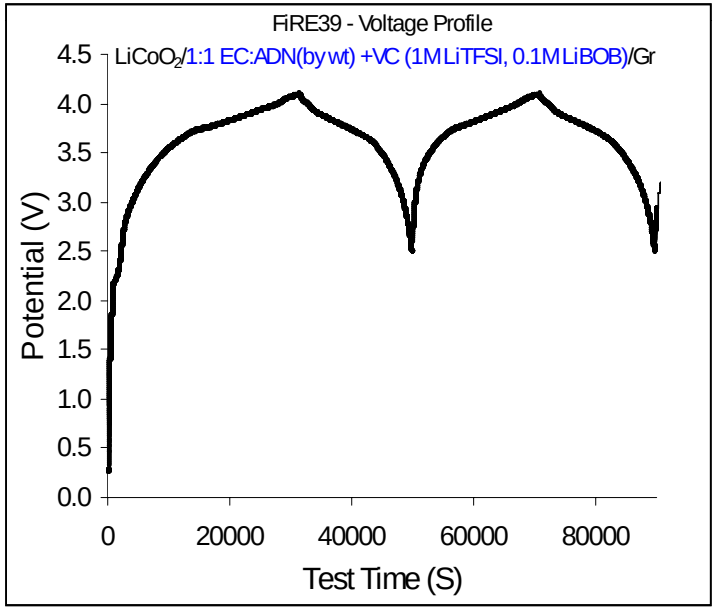
Battery performance: Effect of Vinylidene carbonate (VC) , 2 w.t.% electrolyte additive : EC:ADN

- *VC decreased the discharge capacity of the two electrolytes.*
- *The decrease was more detrimental in the case of the 1:1 as the capacity reached 60 mAh/g by the 50th cycle.*



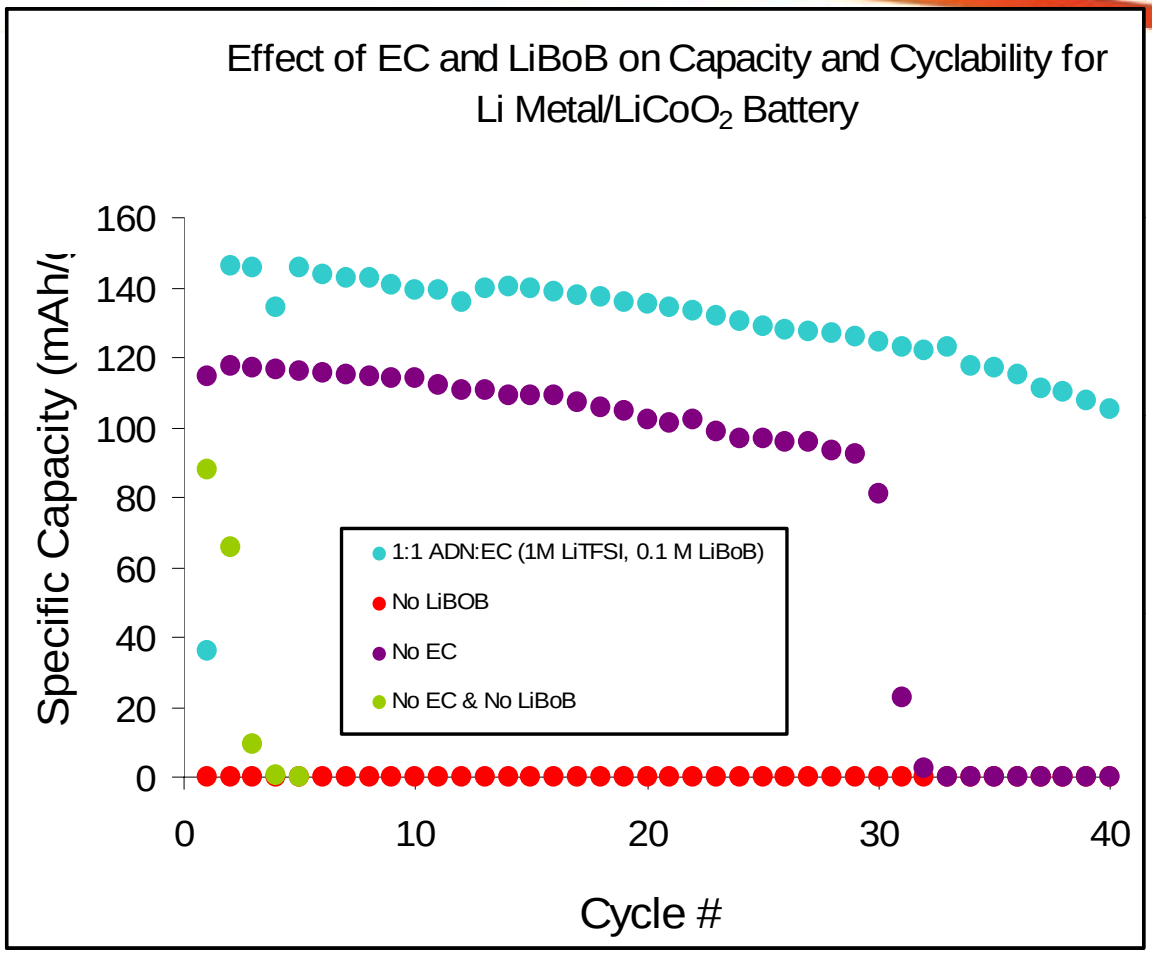






Battery performance: Electrolyte: EC:ADN 1M LiTFSI Electrodes: Graphite/Li Metal

- *Batteries using ADN with no LiBoB or EC do not work.*
- *Batteries using ADN with EC only showed very low capacity.*
- *Batteries using ADN with LiBoB show good capacity of 100-120 mAh/g but they die by the 30th cycle.*
- *Batteries using ADN with EC along with LiBoB gave good capacity.*
- *The 1:1 EC:ADN electrolyte gave initial discharge capacities of 150 mAh/g with gradual loss reaching 105 mAh/g by the 40th cycle.*



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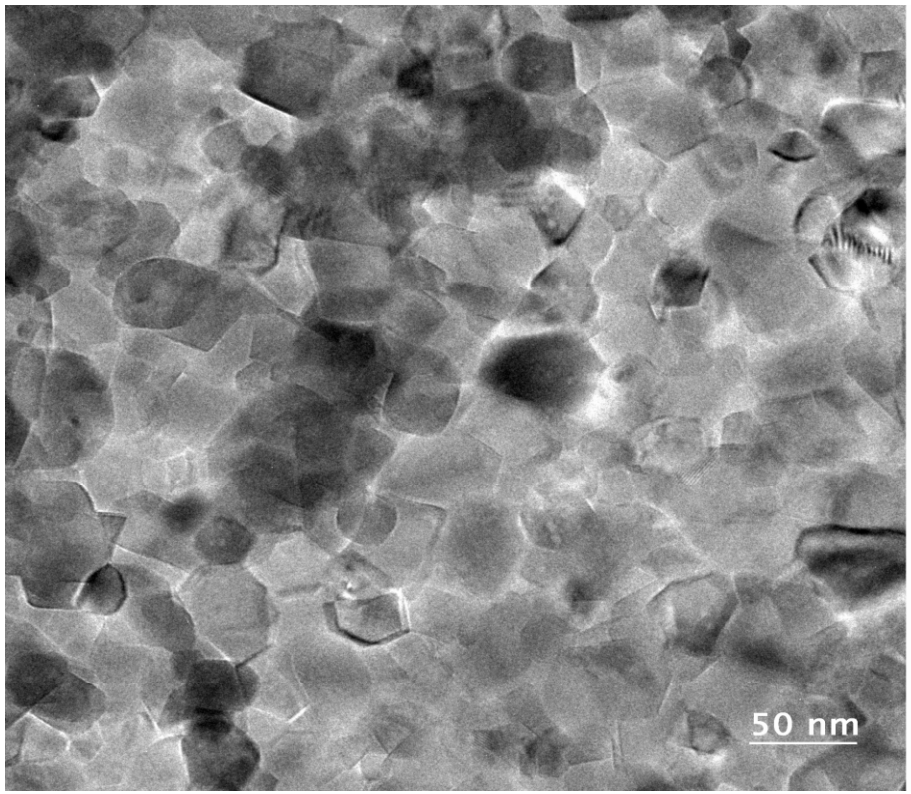
II High voltage nano-cathode material

- *$LiNi_{0.5}Mn_{1.5}O_4$ shows good cycling and high capacity at a high voltage of ~ 4.7 V.*
- *A new method based on the combination of sol-gel and microwave assisted synthesis was developed.*
- *TEM showed that the material has nanoparticles with an average of 40 nm in diameter.*
- *XRD showed a pure phase*



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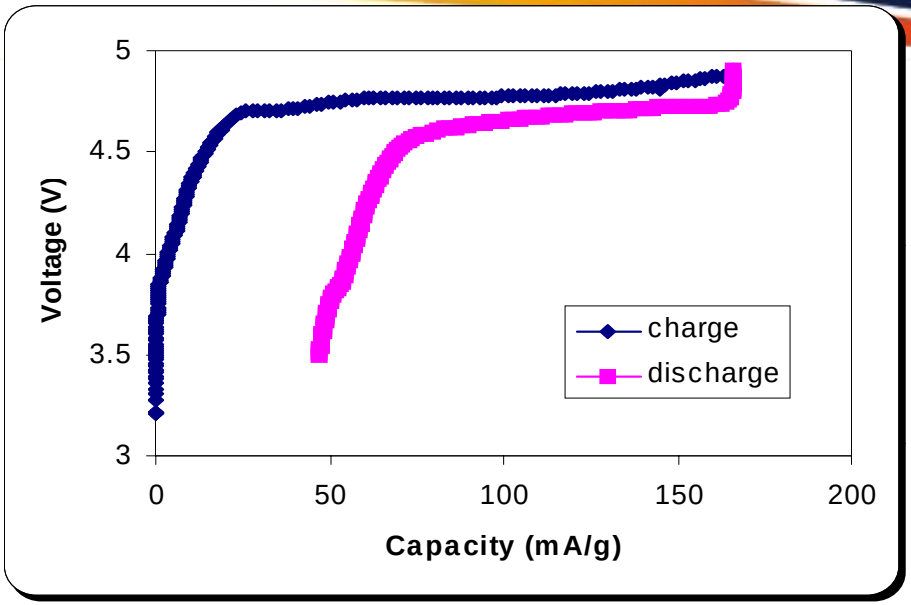
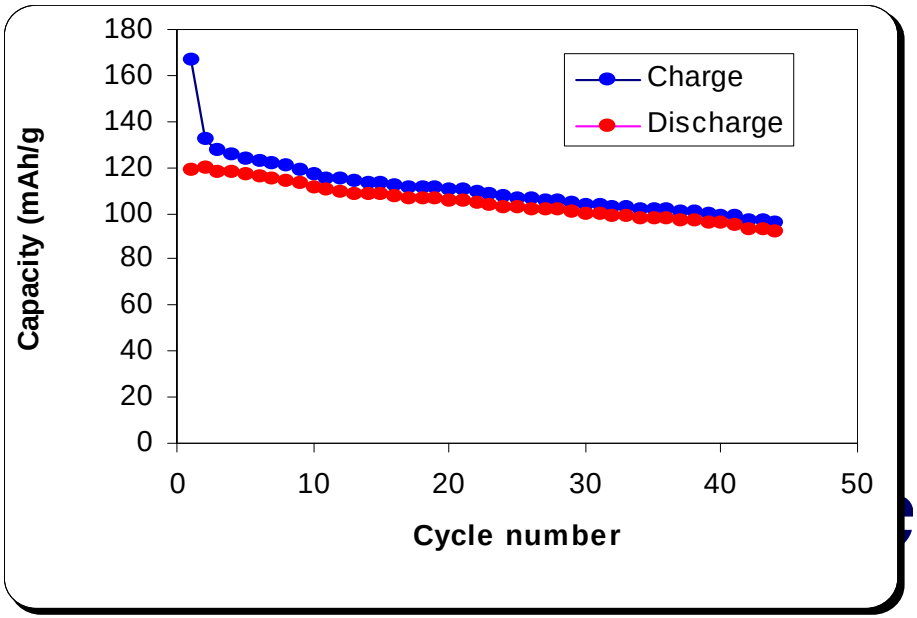
Battery testing of the new nano-cathode

- *Batteries based on the new nano-cathode and Li metal as an anode in a conventional electrolyte showed a first discharge capacity of 118 mAh/g.*
- *The batteries showed moderate capacity retention upon cycling.*
- *Coulombic efficiency improved upon cycling.*





Conclusions

- *We have identified a new family of safer and more electrochemically stable electrolytes that work well in Li-ion batteries.*
- *The electrolyte is based on adiponitrile, a dinitrile solvent which we found that it needs to be coupled with EC as a co-solvent or an additive in order to function in a Li metal or Li-ion battery.*
- *Li-ion batteries using Graphite/$LiCoO_2$ electrodes and the new electrolytes showed capacities reaching 120 mAh/g in the case of 1:1 by volume EC:ADN.*
- *Organic additives were added to the electrolytes and one DP showed improved capacity and cycling while the other VC decreased the capacity.*
- *A 4.7 V $LiNi_{0.5}Mn_{1.5}O_4$ nano-cathode material (40 nm) was prepared and showed improved capacity and cycling.*

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