EXTRACT

Lithium-Ion Batteries and Beyond

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V. Inactive Materials

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2. Separators
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   v. Heat-resistant layer
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Lithium-Ion Battery (LIB): Active and Inactive Materials

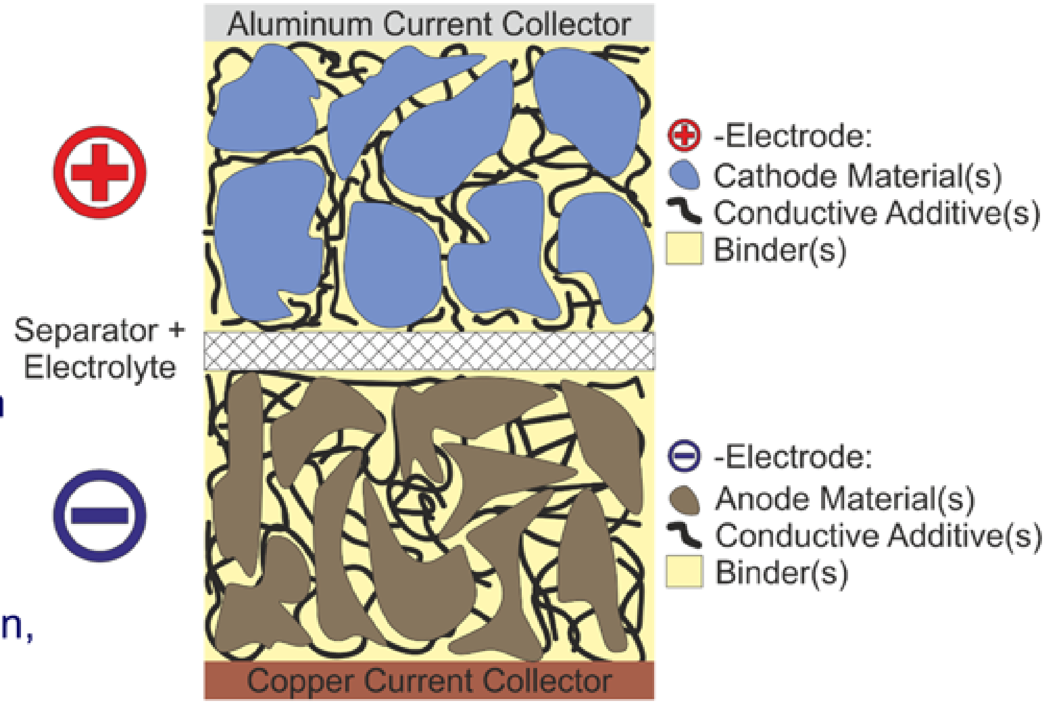
Active Anode and Cathode Materials:
Determine capacity and voltage ⇒ energy

Inactive Materials:
Add, mass + volume ⇒ decrease energy

- **Electrolyte:** ion conduction, interfaces
- **Separator:** safety, electrode separation

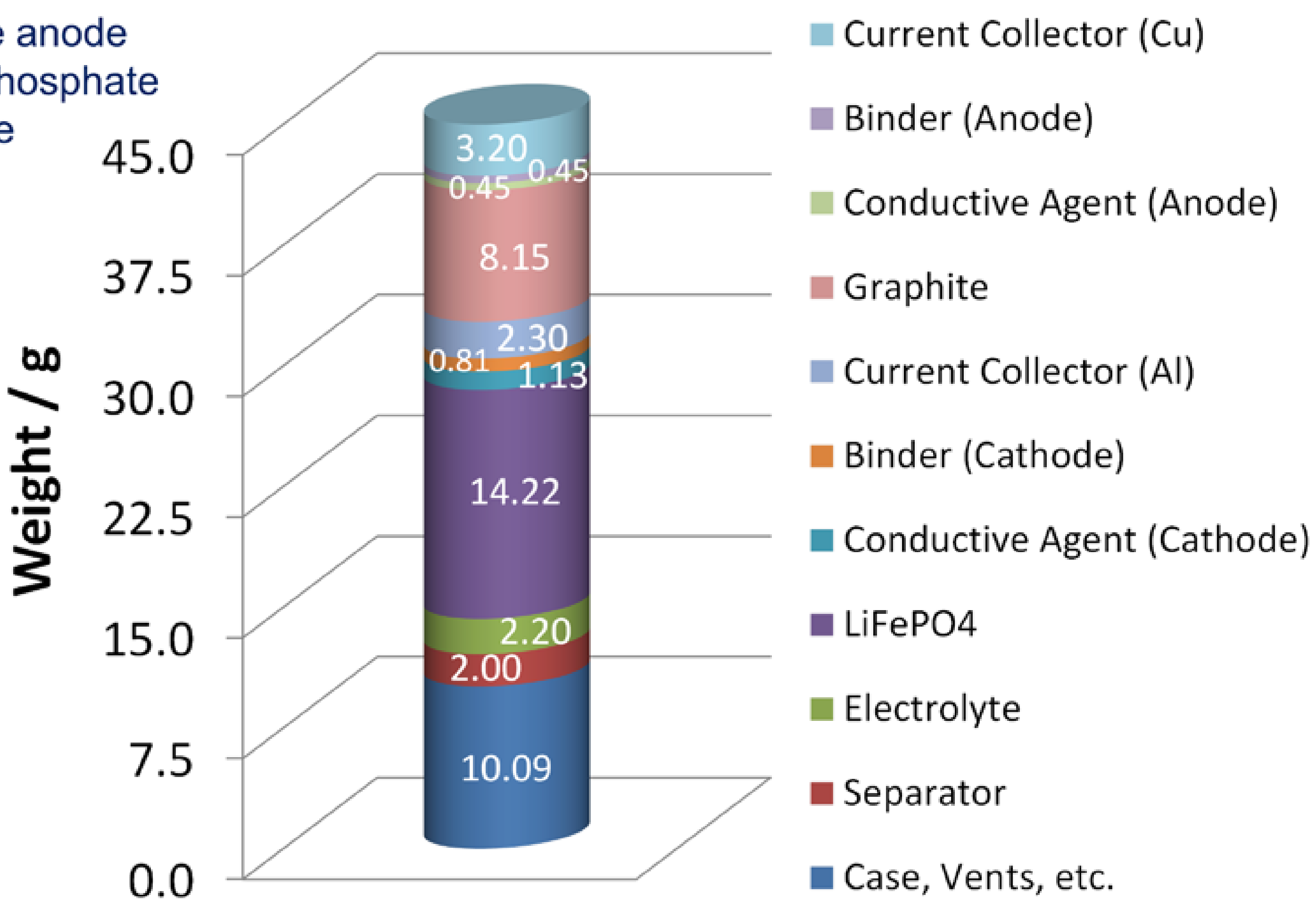
Electrode inactive components:

- **Current collector:** electron conduction, connection to the 'outside'
- **Conductive additive:** porosity, 'inside' electron current distribution
- **Binder:** The 'glue', that holds everything together
- **Processing solvents** (not treated here)

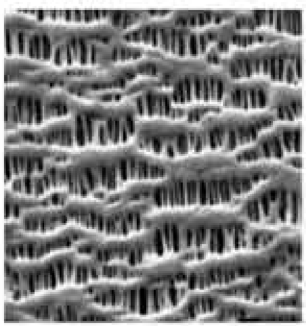
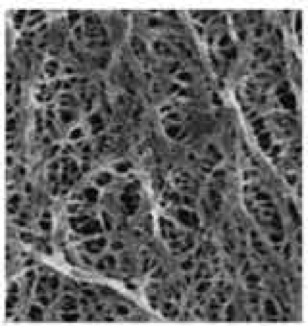
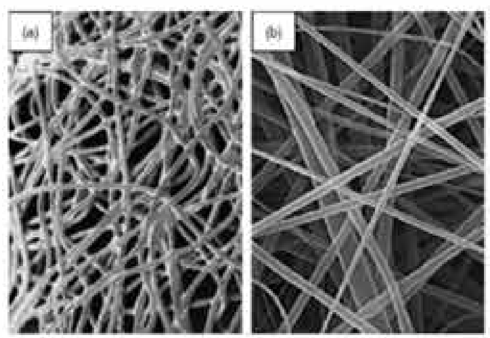
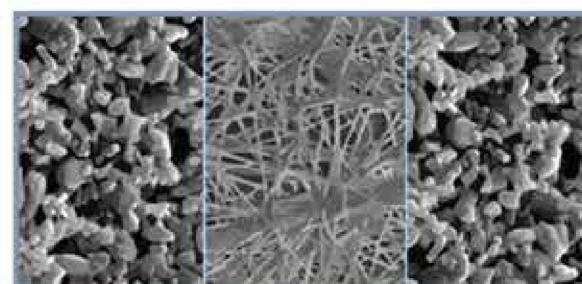


Mass Distribution in an 18650 Cell
Component Details

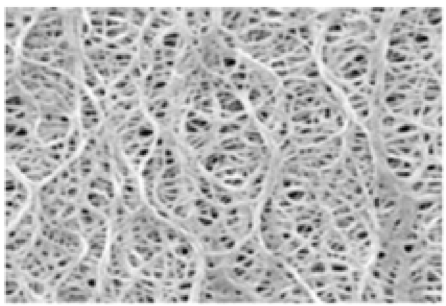
18650 cell: 45g;
based on graphite anode
and lithium-iron-phosphate
($LiFePO_4$) cathode

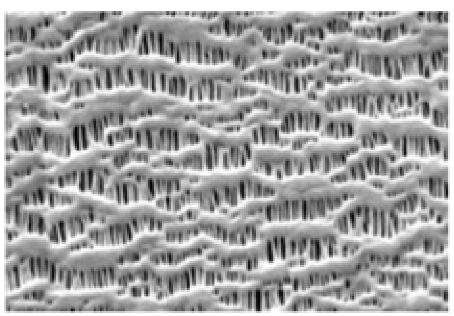


Separator Types

Microporous Polymer Membranes	Non-Woven ("Fleece")	Inorganic Composite Membranes ("Ceramic Separators")
Polyolefines (Polyethylene (PE), Poly-propylene (PP), Single and multi-layers)	e.g., Cellulose, Glass fiber	e.g., Silicate coated polymer
• Thin (ca. 8-30 µm) • Cheap • Medium porosity (ca. 40%) • Standard for Li-Ion (thermal, mechanical) • Thermal shut-down mechanism possible	• Thick (ca. 100-200 µm) • Costs a bit higher • High Porosity (ca. 60-80%), large pores (ca. 20-50 µm) • Excellent electrolyte uptake • Mechanically not stable • Often in primary Li cells	• Better electrolyte wetting • Better thermal stability • Possibility to introduce chemistry which influences cell behavior. • Backbone can be non-woven or polyolefine
 		

Special Separators: Tri-layer, Shut-Down Separators





Shut-down Tri-Layer

- PE, melting temp.: ca.110-140°C
  PP, melting temp.: ca. 150-180°C
- Dry preparation process by lamination
- PP/PE/PP tri-layer used as "shut-down separator“. PE melts and thus stops internal ionic current, while the two PP layers still keep the separating function.
- **Shut-down function** depends on rate of temperature increase, fast thermal runaway, whole separator melts.
- In a series arrangement with high voltage, there is evidence that the higher series voltage will force the current through a separator that has a shut-down
- **Manufacturers, e.g., Celgard, Ube**

Separator Demands: Issues, Accomplishments and To-dos

Thermal stability:

- Melting point depends on polymer chemistry: PET >> PP > PE
- Ceramic coatings have very high melting points
- Search for polymers with higher melting points, e.g. fluorinated polymers

Mechanical stability:

- Wet > dry > non-woven/ceramic
- Depends to a large extent on the preparation process

Electrochemical Stability:

- Polyolefin-based separators have reportedly been unable to withstand very high voltages for long periods of time, e.g., PE is less stable than PP

Chemical Stability:

- Water removal from ceramic separators is necessary for long life
- There is evidence that separators from aged cells contain fluorides from electrolyte

Wettability:

- Low at lower temperatures. Improves with porosity and ceramic content

Cost:

- Single layer (dry) < single layer (wet) < tri-layer and ceramic separator

Stability of the Al Current Collector: Anodic Oxidation and Dissolution; Depending on the Electrolyte Salt

$LiClO_4$, $LiCF_3SO_3$, $LiN(SO_2CF_3)_2$ (= LiTFSI), etc.

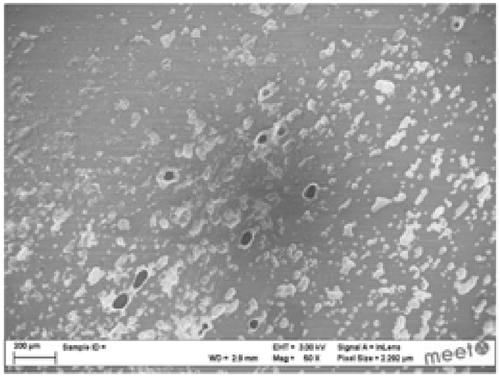
- No significant chemical reaction with Al
  →No effective Al passivation by a chemical reaction!
- Al, as non-noble metal, dissolves by anodic oxidation during electrochemical oxidation **during charge** of the LIB
- Pits are formed by this dissolution process
- This reaction is erroneously called "corrosion", although "corrosion" refers to a process in which no external current or potential is applied

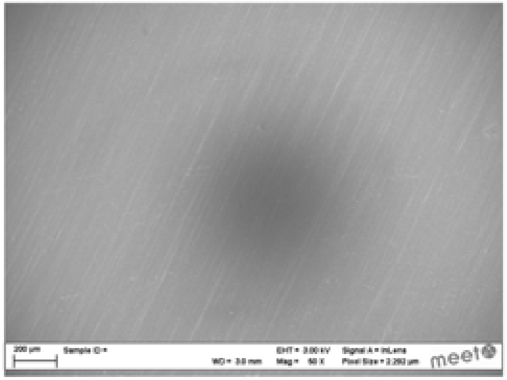
$LiPF_6$, $LiBF_4$, etc.

- Chemically and thermally unstable salts

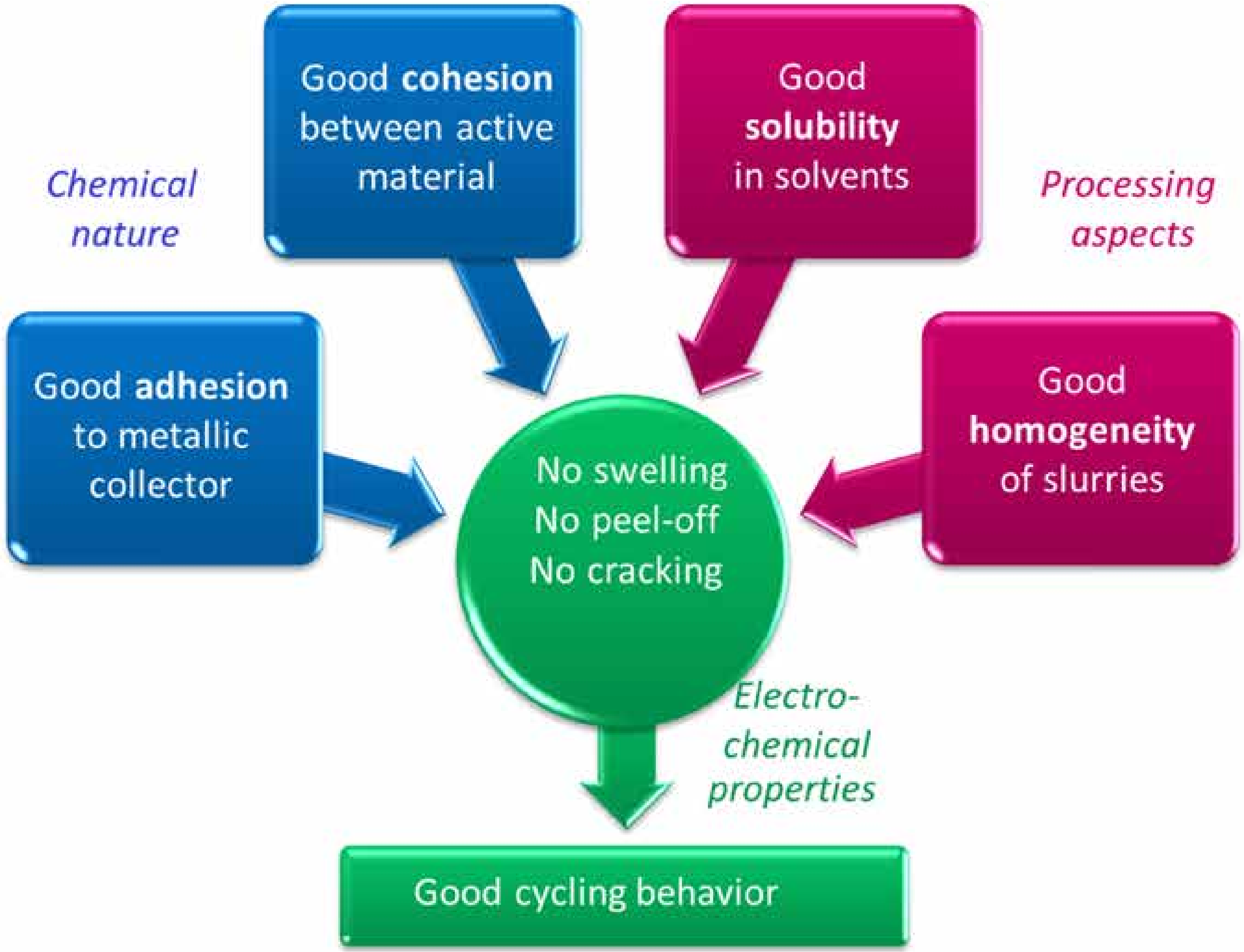
Available with Report purchase

SEM of Al foils after polarization to 4.6 V vs. Li/Li^+ for 24 h
Top: 1M LiTFSI in EC/DMC
Below: 1M $LiPF_6$ in EC/DMC

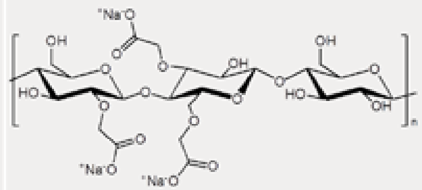
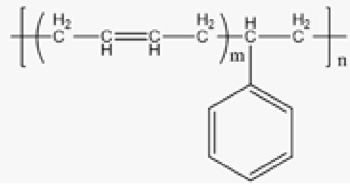
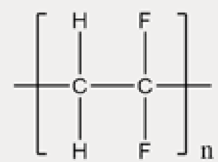
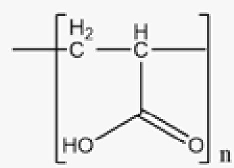




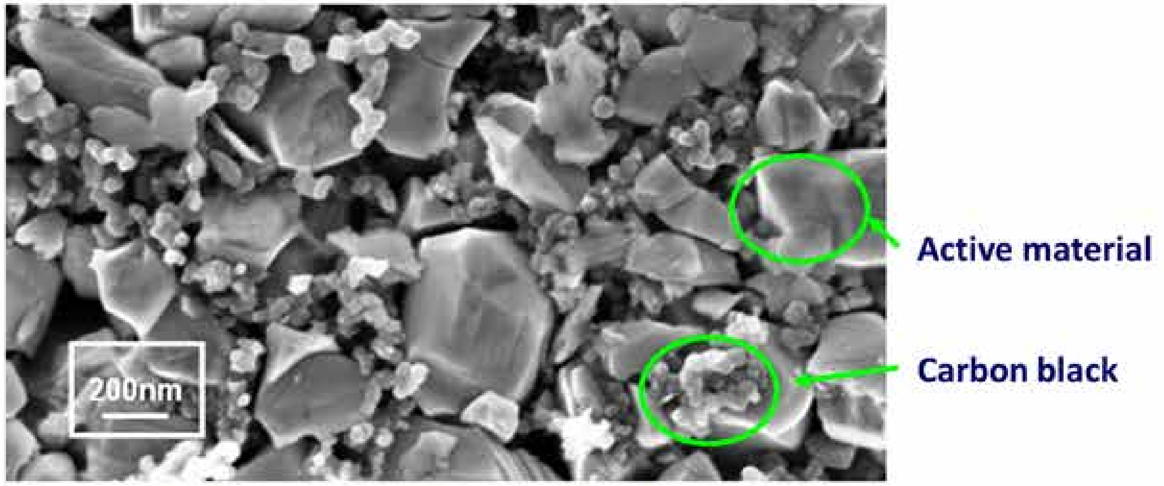
Binders - Key Attributes During Processing



Most Prominent Binders

Binder	Abbrev.	Structure	Advantages
Sodium-carboxymethyl cellulose	Na-CMC or CMC		- Low costs, water soluble
Styrene butadiene rubber	SBR		- High flexibility, water soluble
Poly(vinylidene difluoride)	PVdF		- Good oxidation stability
Polyacrylic acid	PAA		- Water soluble

Introduction: Carbon Black (CB)



Carbon black and active material in cathode

- Improves electronic and thermal conductivity
- Improves performance
- Creates porous electrode structure accessible to electrolyte
- Irreversible reactions with the electrolyte: specific surface area of carbon black is typically >10 times larger than SSA of the cathode material

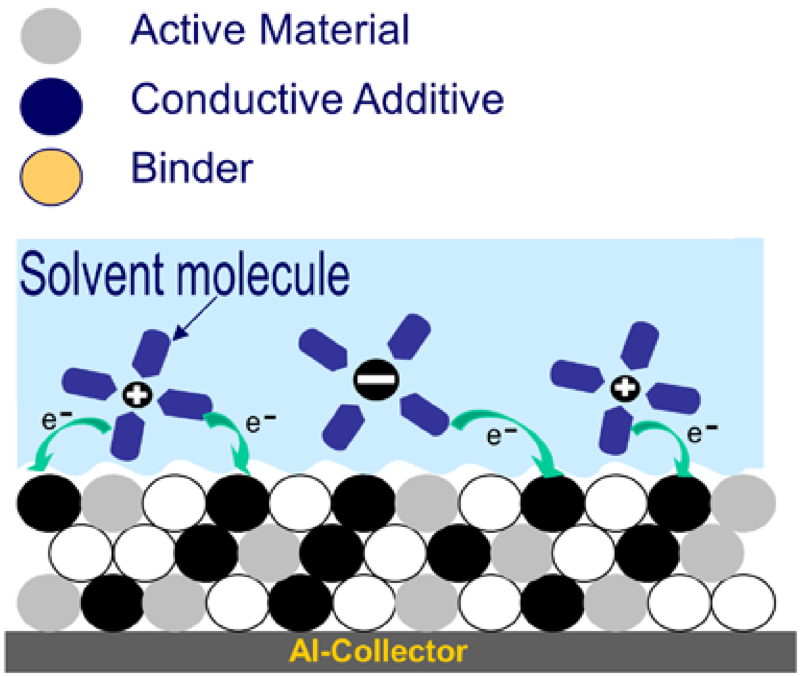
Where Electrolyte Reactions Take Place, e.g., Cathode Side

Electrolyte reactions with the electrode are surface reactions!

Electrolyte reactions and SEI/CEI formation depend on the wetted surface area (in 1st approximation on the BET surface area)*.

BET: Active material: <5 m^2/g (typ.)
BET: Conductive additive: >50m^2/g
10 weight-% of additive may have the same surface impact on electrolyte reactions as 90 weight-% of active material.

BUT: Catalytic activities of materials for electrolyte reactions are different: “Hot Spots” react first, faster, and in a more significant way than the “rest” of the electrode.



"Hot Spots” in the electrode

*MW.; Novák, P.; Monnier, A., *J. Electrochem. Soc.*, **1998**, *145*, 428-436