Getting Materials from Discovery to Production

BATTERY MATERIALS SCALE-UP AND MANUFACTURING RESEARCH

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International Battery Seminar
March 23, 2017
From Discovery to Production

- New materials invented in the Discovery Stage are produced in gram quantities.
- Initial processes may be able to produce material up to 100’s of grams.

-------- Most work stops here --------

- Scaling to kilogram or larger scale usually require substantial process R&D.
- Accurate cost modeling requires optimized manufacturing ready processes.
- Samples are needed for industrial evaluation and for continued R&D.
What We Do

- Develop scalable manufacturing processes.
- Evaluate emerging materials synthesis technologies.
- Develop analytical methods and quality control procedures – establishing materials specifications.
- Make kilogram quantities of the material available for industrial evaluation and further research.
What We Do

- Develop scalable manufacturing processes.
  - Batch – Semi Batch - Continuous

- Evaluate emerging materials synthesis technologies.
  - Continuous Flow Reactors
  - Taylor Vortex Reactors

- Develop analytical methods and quality control procedures – establishing materials specifications.

- Make kilogram quantities of the material available for industrial evaluation and further research.
Scalable Manufacturing Processes

Electrolyte Materials

- Parameters such as time, temperature, stoichiometry, order of addition and solvent are investigated with the aim of increasing yield and product purity.
- Changes in surface to volume ratio means that differences in thermal and mass transfer occur and reactions often need to be re-optimized.

- **Batch**
  - Suited for small production rates or long reaction times.

- **Continuous**
  - Typically used to produce large amounts of product.
The original process have several manufacturing issues:

- Time and energy consuming – a multistep batch process
- Requires multiple solvents
- Generates substantial amount of waste
Process Improvements:
- Process was greatly simplified
- Time was reduced by factor of 4
- Significantly less energy use
- Waste stream was nearly eliminated
- Solvents were eliminated
- The process is environment friendly
- Continuous process developed for large scale manufacturing
Continuous Flow Chemistry

Electrolyte Materials

- The process of moving reactive components in solution through a reactor.
- Enables the continuous synthesis of materials from discovery through process development and production scale.
Continuous Flow Reactors

Key Features and Benefits

- Superior mass and heat transfer improve kinetics, reduces reaction time and results in better selectivity and yield.
- Reaction can be run in conditions not feasible in batch process.
- Improve safety by minimizing volume of active reacting zone.
- Flexible modular design allows for various chemistries and in-line analysis and monitoring.
- Reduced production costs.
Batch vs Flow Reactor Example

Carbonate Solvent Synthesis

- Advanced solvents and additives for electrolytes are needed to allow for:
  - Large electrochemical stability window
  - High ionic conductivity but very low electronic conductivity
  - Low vapor pressure and viscosity at broad temperature range
  - Low flammability (higher flash point)

- MTMSMC is reported to have several of these characteristics, however, the synthesis is difficult by traditional techniques.
  - Low conversion rate
  - Many by-products
  - Difficult to purify

\[
\text{methyl chloroformate} + \text{base} \rightarrow \text{methyl ((trimethylsilyl)methyl) carbonate (MTMSMC)} + \text{HCl}
\]
MTMSMC Synthesis Catalyst Screening

**Batch System**

- Wide variation in catalyst activity.
- Loose correlation with base strength.
- Some acid catalysts also show activity.
- Screening was slow!

Conditions: 2h, 85°C, 5:1 molar ration of DMC: TMSCH₂OH, 1 mol% catalyst, slight nitrogen flow.

Non symmetrical, chlorine free catalytic process
MTMSMC Synthesis Catalyst Screening

Closed Batch System

- Closed system works: The reaction is not entirely an equilibrium process!
- Closed system provide results almost identical to open (ventilated) system.
- Conceivable to develop a flow process.
- Focus on solid catalyst for flow process (no need to remove catalyst after reaction).

Open vs. Closed System

<table>
<thead>
<tr>
<th>Compound</th>
<th>Open System</th>
<th>Closed System</th>
</tr>
</thead>
<tbody>
<tr>
<td>triazadecene</td>
<td>95.0%</td>
<td>98.0%</td>
</tr>
<tr>
<td>DBU</td>
<td>60.0%</td>
<td>65.0%</td>
</tr>
<tr>
<td>Et3N</td>
<td>15.0%</td>
<td>10.0%</td>
</tr>
<tr>
<td>DMAP</td>
<td>70.0%</td>
<td>75.0%</td>
</tr>
<tr>
<td>K3PO4</td>
<td>80.0%</td>
<td>85.0%</td>
</tr>
<tr>
<td>K2CO3</td>
<td>50.0%</td>
<td>45.0%</td>
</tr>
</tbody>
</table>
MTMSMC Synthesis Catalyst Screening

Continuous Flow System

Residence Time: 2 min
MTMSMC Synthesis Catalyst Screening

Continuous Flow System

Residence Time: 4 min
MTMSMC Flow Reactor Synthesis

**First Thoughts:**

- Flow reactor system greatly reduced process R&D time and cost.
  - Shorter reaction time – solvent is run above its boiling point.
  - 10 times faster catalyst screening
- Catalytic Transesterification in a flow reactor system offers green, cost effective process for producing a wide range of advanced electrolyte solvents.

- Other reactions planned:
  - Catalytic Trimethylsilylation
  - Catalytic Hydrosilylation

- Estimated lab scale production rate = 100-200ml per day.
  - Scalability?
Continuous Flow Reactor
But is it scalable?

Scaling out vs Scaling up

Corning Advanced-Flow Reactors

Chemtrix Plantrix Reactors
Cathode Materials
Manufacturing Research
Scalable Manufacturing Processes

Cathode Materials

- Parameters such as time, temperature, stoichiometry, order of addition and reactor mixing are investigated with the aim of improvement of purity, particle morphology, size & distribution and degree of crystallinity.

- Changes in surface to volume ratio means that differences in thermal and mass transfer occur and reactions often need to be re-optimized.

- Batch
  - Labor intensive operations.
  - Batch to batch variability.

- Continuous
  - Product uniformity.
  - Process complexity.
Continuous Stirred Tank Reactor (CSTR)

For cathode precursor co-precipitation

- Flow pattern and degree of mixing is a result of reactor, baffle, impeller design and stirring speed.
  - a lot of variables to optimize!
- Significant changes in surface to volume ratio when scaling.
  - Generating mixing, temperature and feed concentration gradients.
Taylor Vortex Reactor (TVR)
Advanced reactor technology

- Simplified operation
- Product uniformity
- Shorter residence time

Taylor Vortex Flow

Strong centrifugal and Coriolis forces \(\rightarrow\) periodic unstable Taylor vortex flow motion

Homogeneous intense micro-mixing zone: faster reaction kinetics
- High mass and heat transfer: high degree of uniform supersaturation
- Self particle size control: high fluid shear \(\rightarrow\) breakage and re-dispersion
- No dead-zone: improvement of purity, morphology, particle size & distribution, degree of crystallinity

Each unitary vortex cell: enabling micro-mixing

- Key variables affecting fluid motion are hydrodynamic intensity and dimensions of Taylor vortex

From: A. Syed and W.-G. Fishe (2003), Journal of Chemical Technology and Biotechnology 78, 227-235
# Batch vs CSTR vs TVR

## Co-precipitation processes – Batch vs. CSTR vs. TVR

<table>
<thead>
<tr>
<th>Process</th>
<th>Conventional 40L Batch</th>
<th>Advanced 20L CSTR</th>
<th>Taylor Vortex Reactor 1L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis condition</td>
<td>Precursors were obtained after 24hr operation at reaction temp. = 33°C and NH₄OH/TM = 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcined material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIB-SEM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Degree of opt.</td>
<td>Initial optimization</td>
<td>Optimized</td>
<td>Preliminary</td>
</tr>
<tr>
<td>Morphology</td>
<td>Non-spherical to quasi-spherical</td>
<td>Quasi-spherical to spherical</td>
<td>Spherical</td>
</tr>
<tr>
<td>ICP-MS analysis</td>
<td>Li₁₀.⁶⁷Ni₀.⁶¹Mn₀.₃₃Co₀.₀₆O₇</td>
<td>Li₁₀.⁶₅Ni₀.₆¹Mn₀.₃₃Co₀.₀₆O₇</td>
<td>Li₁₀.⁷₃Ni₀.₆₀Mn₀.₃₄Co₀.₀₆O₇</td>
</tr>
<tr>
<td>BET [m²/g]</td>
<td>0.71</td>
<td>0.53</td>
<td>0.46</td>
</tr>
<tr>
<td>PSA [µm]</td>
<td>3.9 / 13.0 / 19.9</td>
<td>6.4 / 11.2 / 19.7</td>
<td>8.9 / 15.1 / 25.9</td>
</tr>
<tr>
<td>Tap den. [g/cc]</td>
<td>1.25 initial optimization → 1.73</td>
<td>1.39 optimization → 2.06</td>
<td>2.04 (first run)</td>
</tr>
<tr>
<td>1st DC [mAh/g]</td>
<td>200.0</td>
<td>203.4</td>
<td>198.0</td>
</tr>
</tbody>
</table>
NCM 811
Commercial CSTR vs Lab TVR

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Results</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size Distribution</td>
<td>D10 (µm)</td>
<td>7.35</td>
</tr>
<tr>
<td></td>
<td>D50 (µm)</td>
<td>13.77</td>
</tr>
<tr>
<td></td>
<td>D90 (µm)</td>
<td>24.88</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>0.37</td>
<td>BET</td>
</tr>
<tr>
<td>Tap Density (g/cc)</td>
<td>2.51</td>
<td>Tap Density Meter</td>
</tr>
</tbody>
</table>

Element mol %
- Li / (Ni+Co+Mn) 1.04
- Ni / (Ni+Co+Mn) 0.796
- Co / (Ni+Co+Mn) 0.102
- Mn / (Ni+Co+Mn) 0.102

Analysis Results Method

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<td>D50 (µm)</td>
<td>14.01</td>
</tr>
<tr>
<td></td>
<td>D90 (µm)</td>
<td>23.94</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>0.40</td>
<td>BET</td>
</tr>
<tr>
<td>Tap Density (g/cc)</td>
<td>2.428</td>
<td>Tap Density Meter</td>
</tr>
</tbody>
</table>

Element mol %
- Li / (Ni+Co+Mn) 0.972
- Ni / (Ni+Co+Mn) 0.797
- Co / (Ni+Co+Mn) 0.102
- Mn / (Ni+Co+Mn) 0.101

ICP-MS
Taylor Vortex Reactor

But is it scalable?

20 mL TVR

1,000L TVR – 240 kg or more per day
Scalability Evaluation In Progress

Cathode Synthesis and Scalability Evaluation

- Investigating a range of cathode chemistries for physical and electrochemical performance.
- Investigating synthesis with dopants and coatings.

1L TVR – 10 g/hr
(1cm reaction zone)

10L TVR – 100 g/hr
(2cm reaction zone)

40L TVR – 400 g/hr
(2.5cm reaction zone)
In Summary

Emerging Materials Synthesis Technologies

- The Taylor vortex reactor
  - Provide more powerful and uniform mixing, precise temperature control, improved reaction control resulting in reduced process optimization.

- Continuous flow reactors
  - Improved thermal management, enhanced mixing control and access to larger operating windows (reaction time, temperature & pressure).

Both technologies provide opportunities for a faster path to scalable materials production.

Production scale costs still need to be evaluated.
ACKNOWLEDGEMENTS

Support from David Howell and Peter Faguy of the U.S. Department of Energy’s Vehicle Technologies Office and David Hardy from the Advanced Manufacturing Office is gratefully acknowledged.

- The Materials Engineering Research Facility Staff:
  - Youngho Shin
  - Ozge Feridun
  - Kris Pupek
  - Trevor Dzwiniel
  - James Ciszewski
  - Eva Allen
  - Lisa Berkland
  - Gerald Jeka
  - Michael Kras
  - Michael Furlan
  - Scott Lockwood

For samples and further information: [www.anl.gov/merf](http://www.anl.gov/merf)
Argonne’s Material Engineering Research Facility

Bridging the Gap Between Research and Commercialization

- Decrease tech to market time.
- Enables commercial evaluation of new materials and accurate cost modeling.
- Evaluation of emerging materials manufacturing technologies can decrease time, help lower costs and improve materials.
- Samples are available.

Bench Labs

Pilot Labs

Highbay Space
Argonne’s Material Engineering Research Facility
Working with Universities, National Labs and Industry
Thank You