# International Battery Association (IBA) and Pacific Power Source Symposium 2015 Joint Meeting

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<thead>
<tr>
<th>Time</th>
<th>Mon 1/5/2015</th>
<th>Tue 1/6/2015</th>
<th>Wed 1/7/2015</th>
<th>Thu 1/8/2015</th>
<th>Fri 1/9/2015</th>
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<tbody>
<tr>
<td>7:30</td>
<td>Registration / Continental Breakfast (Kohala 2)</td>
<td>Registration / Continental Breakfast (Kohala 2)</td>
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<td>8:20</td>
<td>Opening Remarks</td>
<td>Registration / Continental Breakfast (Kohala 2)</td>
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<tr>
<td>8:30</td>
<td>Chair: Michael Thackeray</td>
<td>Chair: Robert Kostecki</td>
<td>Chair: Arumugam Manthiram</td>
<td>Chair: Gerbrand Ceder</td>
<td>Chair: Adam Best</td>
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<td>9:00</td>
<td>Robert Huggins</td>
<td>Peter Faguy</td>
<td>Peter Bruce</td>
<td>Doron Aurbach</td>
<td>Dominique Guyomard</td>
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<td>9:25</td>
<td>Stan Whittingham</td>
<td>Christopher Orendorff</td>
<td>Steven Visco</td>
<td>Jason Croy</td>
<td>Kristina Edström</td>
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<td>9:45</td>
<td>Yi Cui</td>
<td>Ralph Brodd</td>
<td>Steven Renault</td>
<td>Hilmi Buqa</td>
<td>Zhengcheng Zhang</td>
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<td>10:05</td>
<td>Coffee Break (Kohala 2)</td>
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<td>10:05</td>
<td>Chair: Yi Cui</td>
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<td>Chair: Peter Bruce</td>
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<td>Chair: Kristina Edström</td>
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<td>10:30</td>
<td>Jeff Chamberlain</td>
<td>Khalil Amine</td>
<td>Arumugam Manthiram</td>
<td>Gerbrand Ceder</td>
<td>Adam Best</td>
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<td>10:55</td>
<td>Zempachi Ogumi</td>
<td>Xueliang Andy Sun</td>
<td>Won-Sub Yoon</td>
<td>Laurence Croguennec</td>
<td>Zhiyi Jiang</td>
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<td>11:15</td>
<td>Margret Wohlfahrt-Mehrens</td>
<td>Joel Gauicher</td>
<td>Maria Chan</td>
<td>Marca Doeff</td>
<td>Chong Min Koo</td>
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<td>11:35</td>
<td>Anthony Burrell</td>
<td>Yong Yang</td>
<td>Phuti Ngoepe</td>
<td>Flaviano Garcia Alvarado</td>
<td>Neeraj Sharma</td>
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<tr>
<td>11:55</td>
<td>Lunch (Kohala 4)</td>
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<td>13:30</td>
<td>Chair: Stan Whittingham</td>
<td>Chair: Khalil Amine</td>
<td>Chair: John Muldoon</td>
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<tr>
<td>14:00</td>
<td>Michael Thackeray</td>
<td>Martin Winter</td>
<td>Linda Nazar</td>
<td>Jud Virden</td>
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<td>14:25</td>
<td>Yet-Ming Chiang</td>
<td>Atsuo Yamada</td>
<td>Jun Liu</td>
<td>Maria Forsyth</td>
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<td>14:45</td>
<td>Martha Maly-Schreiber</td>
<td>Patrick Howlett</td>
<td>Karim Zaghib</td>
<td>George Blomgren</td>
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<td>15:05</td>
<td>Anthony Petric</td>
<td>Alexey Serov</td>
<td>Kristin Persson</td>
<td>Wei Wang</td>
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<td>15:05</td>
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<td>15:30</td>
<td>Xiao-Qing Yang</td>
<td>Takeshi Abe</td>
<td>John Muldoon</td>
<td>Vincent Sprekle</td>
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<td>15:55</td>
<td>Jeffrey Wolfenstine</td>
<td>Robert Kostecki</td>
<td>Ratnakumar Bugga</td>
<td>Chunmei Ban</td>
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<td>16:15</td>
<td>Nae-Lih Wu</td>
<td>Tetsuya Osaka</td>
<td>Zheng Li</td>
<td>Cyril Truchot</td>
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<td>16:35</td>
<td>Minoru Inaba</td>
<td>Fabio Rosciano</td>
<td>Wu Xu</td>
<td>Ira Bloom</td>
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<tr>
<td>16:55</td>
<td>A Special Moment for Robert A. Huggins</td>
<td>Yoshiharu Uchimoto</td>
<td>Lawrence Ebert</td>
<td>Arnaud Devie</td>
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<tr>
<td>17:15</td>
<td>Symposium Dinner in honor of Professor Robert A. Huggins (Palm Terrace)</td>
<td>Poster Session</td>
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<td>18:00</td>
<td>Reception (Grand Staircase)</td>
<td>Poster Session</td>
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<td>20:30</td>
<td>IBA Board Meeting (Kohala Ballroom Foyer)</td>
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2015 IBA-PPSS JOINT MEETING
TECHNICAL PROGRAM
<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>8:30</td>
<td>Robert Huggins</td>
<td>Prussian blue structure materials with rapid kinetics and long cycle life for grid scale energy storage</td>
</tr>
<tr>
<td>9:00</td>
<td>Stan Whittingham</td>
<td>Two Li intercalation cathodes as an alternative to Mg intercalation</td>
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<tr>
<td>9:25</td>
<td>Yi Cui</td>
<td>TBA</td>
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<tr>
<td>9:45</td>
<td>Claude Delmas</td>
<td>The P2-Nax(Fe,Mn)O2 layered oxides in Na-batteries</td>
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<tr>
<td>10:30</td>
<td>Jeff Chamberlain</td>
<td>TBA</td>
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<tr>
<td>11:15</td>
<td>Margret Wohlfahrt-Mehrens</td>
<td>High voltage cathode materials for lithium ion batteries - from materials to complete cells</td>
</tr>
<tr>
<td>11:35</td>
<td>Anthony Burell</td>
<td>TBA</td>
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<tr>
<td>13:00</td>
<td>Michael Thackeray</td>
<td>High-energy cathode research at Argonne National Laboratory</td>
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<tr>
<td>14:00</td>
<td>Yet-Ming Chiang</td>
<td>Electrochemical storage via reversible metal sulfide precipitation</td>
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<tr>
<td>14:25</td>
<td>Martha Maly-Schreiber</td>
<td>Is there a relationship between batteries and foodstuffs?</td>
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<tr>
<td>14:45</td>
<td>Anthony Petric</td>
<td>Ellingham revisited</td>
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<tr>
<td>15:00</td>
<td>Xiao-Qing Yang</td>
<td>Using synchrotron based X-ray diffraction and absorption and TXM to study the new electrode materials for next generation of batteries</td>
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<tr>
<td>15:30</td>
<td>Jeffrey Wolfenstine</td>
<td>TBA</td>
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<tr>
<td>16:15</td>
<td>Nae-Lih Wu</td>
<td>Mechanically robust and highly ion-conductive polymer-blend artificial SEI for high-power and long-life lithium-ion battery anodes</td>
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<tr>
<td>16:35</td>
<td>Minoru Inaba</td>
<td>New titanium dioxide high potential negative electrodes</td>
</tr>
<tr>
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<tr>
<td>8:30</td>
<td>Peter Faguy</td>
<td>From the glove box to the garage - executing on the promise of next-generation lithium ion battery materials: the Applied Battery Research portfolio at the Office of Energy Efficiency and Renewable Energy</td>
</tr>
<tr>
<td>9:00</td>
<td>Christopher Orendorff</td>
<td>Comprehensive understanding of battery safety</td>
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<tr>
<td>9:25</td>
<td>Ralph Brodd</td>
<td>Additives to extend the life of lead acid batteries</td>
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<tr>
<td>9:45</td>
<td>Matthieu Dubarry</td>
<td>Two-point state-of-charge determination in lithium-ion battery packs</td>
</tr>
<tr>
<td>10:30</td>
<td>Khalil Amine</td>
<td>A new high energy battery system based on SeSx (x=0-7)</td>
</tr>
<tr>
<td>10:55</td>
<td>Xueliang (Andy) Sun</td>
<td>Designing surface and interface of electrodes for Li ion batteries</td>
</tr>
<tr>
<td>11:15</td>
<td>Joel Gaubicher</td>
<td>Conducting polymer additives for millimetric thick electrodes of Li batteries</td>
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<tr>
<td>11:35</td>
<td>Yong Yang</td>
<td>Modulation of the interfacial properties of electrode with functional electrolyte additives for Li-ion batteries</td>
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<tr>
<td>13:30</td>
<td>Martin Winter</td>
<td>Novel electrolyte components enabling high voltage lithium ion batteries</td>
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<tr>
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<td>Atsuo Yamada</td>
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<tr>
<td>14:25</td>
<td>Patrick Howlett</td>
<td>Ionic liquid electrolytes for sodium battery applications – a study of the effect of concentration and temperature on sodium transport and electrochemical behaviour</td>
</tr>
<tr>
<td>14:45</td>
<td>Alexei Serov</td>
<td>Energy storage materials derived by sacrificial support method</td>
</tr>
<tr>
<td>15:30</td>
<td>Takeshi Abe</td>
<td>TBA</td>
</tr>
<tr>
<td>15:55</td>
<td>Robert Kostecki</td>
<td>Chemical imaging of interfaces and interphases in Li-ion anodes</td>
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<tr>
<td>16:15</td>
<td>Tetsuya Osaka</td>
<td>New proposal on diagnostic methods for commercial lithium-ion batteries through electrochemical impedance spectroscopy</td>
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<tr>
<td>16:35</td>
<td>Fabio Rosciano</td>
<td>High-voltage solid-solid interface properties of LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
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<tr>
<td>16:55</td>
<td>Yoshiharu Uchimoto</td>
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**Wednesday, January 7, 2015**

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<tr>
<th>Time</th>
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<tr>
<td>8:30</td>
<td>Peter Bruce</td>
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<tr>
<td>9:00</td>
<td>Steven Visco</td>
<td>TBA</td>
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<tr>
<td>9:25</td>
<td>Steven Renault</td>
<td>Lithium carboxylates for LiBs: life, death and rise of the phoenix</td>
</tr>
<tr>
<td>9:45</td>
<td>Matthieu Morcrette</td>
<td>New insights into Li-S batteries</td>
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<tr>
<td>10:30</td>
<td>Arumugam Manthiram</td>
<td>High-energy, long-life lithium-sulfur batteries</td>
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<tr>
<td>10:55</td>
<td>Won-Sub Yoon</td>
<td>Deciphering the thermal behavior of lithium rich cathode material for lithium-ion batteries by synchrotron-based X-ray techniques</td>
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<tr>
<td>11:15</td>
<td>Maria Chan</td>
<td>First principles study of high capacity electrode/electrocatalyst materials for hybrid lithium-ion/lithium-oxygen cells</td>
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<tr>
<td>11:35</td>
<td>Phuti Ngoepe</td>
<td>Mechanical properties changes and voltage profiles in nanostructured MnO₂</td>
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<tr>
<td>13:30</td>
<td>Linda Nazar</td>
<td>TBA</td>
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<tr>
<td>14:00</td>
<td>Jun Liu</td>
<td>TBA</td>
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<tr>
<td>14:25</td>
<td>Karim Zhagib</td>
<td>HQ R&amp;D on silicon anode for high energy Li-ion batteries: nano vs micron</td>
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<tr>
<td>14:45</td>
<td>Kristin Persson</td>
<td>Solvation structure of multi-valent ions for multivalent battery applications and its implications for stability and charge transfer</td>
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<tr>
<td>15:30</td>
<td>John Muldoon</td>
<td>Challenges in Mg battery</td>
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<td>Ratnakumar Bugga</td>
<td>TBA</td>
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<tr>
<td>16:15</td>
<td>Zheng Li</td>
<td>Issues and challenges of aqueous rechargeable sodium-ion batteries with intercalation electrodes</td>
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<tr>
<td>16:35</td>
<td>Wu Xu</td>
<td>Advanced redox flow battery technologies</td>
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<tr>
<td>16:55</td>
<td>Lawrence Ebert</td>
<td>Patents and batteries: something old and something new</td>
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<tr>
<td>Time</td>
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<tr>
<td>8:30</td>
<td>Doron Aurbach</td>
<td>Electrolyte solutions for advanced batteries (high voltage Li ion, Li-s, Li-oxygen &amp; Mg)</td>
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<tr>
<td>9:00</td>
<td>Jason Croy</td>
<td>High-energy cathode research at Argonne National Laboratory</td>
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<tr>
<td>9:25</td>
<td>Hilmi Buqa</td>
<td>Water based binder electrodes for highly-safe and lifetime-stable titanate Li-ion batteries</td>
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<tr>
<td>9:45</td>
<td>Torbjorn Gustafsson</td>
<td>Lithium iron sulfate fluoride synthesis, structure and function</td>
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<tr>
<td>10:30</td>
<td>Gerbrand Ceder</td>
<td>How to achieve near theoretical capacity in cathodes</td>
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<tr>
<td>10:55</td>
<td>Laurence Crogueuenec</td>
<td>Na$_3$V$_2$(PO$_4$)$_2$F$_3$, a positive electrode material of high interest for Na-ion batteries</td>
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<tr>
<td>11:15</td>
<td>Marca Doeff</td>
<td>Overcoming practical obstacles to the use of garnet LLZO solid electrolytes in lithium batteries</td>
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<tr>
<td>11:35</td>
<td>Flaviano Garcia Alvarado</td>
<td>Titanates and related materials as negative electrodes for sodium-ion batteries: A$_2$Ti$<em>6$O$</em>{13}$ and TiO$_2$ hollandite</td>
</tr>
<tr>
<td>13:30</td>
<td>Jud Virden</td>
<td>Grid energy storage update – what’s new!</td>
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<tr>
<td>14:00</td>
<td>Maria Forsyth</td>
<td>Ionic liquid electrolytes for sodium battery applications – a study of the effect of concentration and temperature on sodium transport and electrochemical behaviour</td>
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<td>Advanced redox flow battery technologies</td>
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<td>15:30</td>
<td>Vincent Sprenkle</td>
<td>All vanadium redox flow battery development for stationary energy storage applications</td>
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<tr>
<td>15:55</td>
<td>Chunmei Ban</td>
<td>In-situ investigation of atomic/molecular layer deposition coatings towards a better understanding of their effect on electrochemical performance</td>
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<tr>
<td>16:15</td>
<td>Cyril Truchot</td>
<td>Testing and performance of a next generation of aqueous hybrid ion battery for large format stationary energy storage device</td>
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<tr>
<td>16:35</td>
<td>Ira Bloom</td>
<td>Effect of fast charging on lithium-ion cells: performance and post-test results</td>
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<tr>
<td>16:55</td>
<td>Arnaud Devie</td>
<td>Energy density: from half cells to full cell</td>
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### Friday, January 9, 2015

<table>
<thead>
<tr>
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<th>Speaker</th>
<th>Topic</th>
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<tbody>
<tr>
<td>8:30</td>
<td>Dominique Guyomard</td>
<td>Multi-direction optimization of Si-based negative electrodes for Li-ion batteries</td>
</tr>
<tr>
<td>9:00</td>
<td>Kristina Edstrom</td>
<td>HAXPES and HPXPS – some examples of interfacial reactions in Li-based batteries</td>
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<tr>
<td>9:25</td>
<td>Zhengcheng Zhang</td>
<td>Improved performance of lithium-sulfur battery with fluorinated electrolyte</td>
</tr>
<tr>
<td>9:45</td>
<td>She-Huang Wu</td>
<td>Lithium-ions migration in Li$_4$Ti$_5$O$_12$ studied by using in-situ neutron powder diffraction</td>
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<tr>
<td>10:30</td>
<td>Adam Best</td>
<td>Developing electrolytes F.A.S.T.E.R</td>
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<tr>
<td>10:55</td>
<td>Zhiyi Jiang</td>
<td>High power lithium-ion cells for automotive applications</td>
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<td>11:15</td>
<td>Chong Min Koo</td>
<td>Hybrid polysilsesquioxane ionogel electrolytes for high temperature lithium batteries</td>
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<tr>
<td>11:35</td>
<td>Neeraj Sharma</td>
<td>Probing electrochemistry and crystal structure simultaneously inside batteries while they function</td>
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### POSTER SESSION: WEDNESDAY AND THURSDAY

<table>
<thead>
<tr>
<th>18:00</th>
<th>Laurence Croguennec</th>
<th>Operando neutron diffraction studies of Li-ion battery electrodes</th>
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<tbody>
<tr>
<td></td>
<td>Adam Best</td>
<td>S/PPy composite cathodes for Li-S batteries prepared by facile in-situ 2-step electropolymerisation process</td>
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<td>Marzi Barghamadi</td>
<td>Investigating the effects of LiNO₃ and ionic liquids on SEI layer formation and stability in Li-S batteries</td>
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<td>Stéven Renault</td>
<td>Dilithium (2, 5-dilithium-oxy)-terephthalate (Li₄C₈H₂O₆) as a novel organic catalyst for Li-O₂ battery</td>
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<td></td>
<td>Chengjun Xu</td>
<td>Multivalent ion battery chemistry: new rechargeable zinc ion and nickel ion batteries</td>
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<td></td>
<td>Yuki Orikasa</td>
<td>Recent development of magnesium rechargeable battery using polyanion compound cathode and inorganic electrolyte</td>
</tr>
<tr>
<td></td>
<td>Titus Masese</td>
<td>Phase Transition between Li₂FeSiO₄ and LiFeSiO₄ at Room and Elevated Temperature</td>
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</table>
A significant effort is underway at the moment to develop safe advanced high energy density storage system with long cycle life, and low cost for grid and electric vehicle applications. To achieve this goal, new battery system with energy densities two to three times greater than conventional lithium ion batteries is needed. In 2012, our group reported for the first time that selenium and selenium-sulfur could be cycled versus both lithium and sodium.[1,2] The choice of selenium, which is a d-electron containing element of group 16 in the periodic table, is due to a) its higher electrical conductivity compared to sulfur, and b) its high theoretical gravimetric capacity (678 mA·h/g) and volumetric capacity (3268 mA·h/cm$^3$).

Our recently results demonstrate that the Li/SeS$\pm x$ cell performance is significantly improved in terms of voltage profile and Columbic efficiency with the adoption of an ether-based electrolyte. The voltage profiles of these cells show that in ether based electrolyte, complete lithiation of selenium to Li$_2$Se is occurring through multi-step reactions, which indicate the possible formation of intermediate phases. This conclusion was confirmed by advanced characterization techniques including synchrotron high-energy X-ray diffraction (HEXRD) and X-ray absorption spectroscopy (XAS), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). In-situ synchrotron XAS measurement clearly shows the difference of the Li-Se cells using ether- or carbonate-based electrolytes, (Fig. 1(a) and (b)). In the ether-based electrolyte, selenium is reduced into lithium polyselenides first, and then further reduced to Li$_2$Se. The observation of Li$_2$Se on the cycled Li foil anode by Raman spectra confirmed the formation of soluble polyselenides in the ether-based electrolyte, which leads to the shuttle effect as in the Li-S system hence the formation of Li$_2$Se on Li anode. However, in carbonate-based electrolyte, selenium is directly reduced to Li$_2$Se without any intermediate phase formation. Solubility test of Se, Li$_2$Se and Li$_2$S shows no dissolution take place when using carbonate solvents, suggesting that the solubility of the redox products dominates the reaction mechanism of this battery system. These results demonstrated that the cell performance based on Se or SeS$_x$ system highly depends on the nature of the electrolyte.

Reference
Fig. 1 Derivative of normalized in-situ XANES spectra of Li-Se cells in (a) ether-based electrolyte, and (b) carbonate-based electrolyte, with voltage profile inserted correspondingly.

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While main properties of batteries are determined by the electrode materials, the existential question of: will work or not, depends strongly on the nature of the electrolyte solutions. The operation of all kinds of Li batteries depends on complicated passivation phenomena, because there is no way to match to the relevant electrodes, electrolyte solutions with which they are thermodynamically stable. Fortunately, surface films based on ionic Li compounds may behave as SEI, thus enabling free Li ions migration through them. Turning to Mg batteries, passivation phenomena are forbidden, because they should always block transport of Mg ions. In this presentation the focus is on some interesting electrolyte solutions for advanced batteries. The operation of high capacity Li-silicon anodes requires the use of solutions that form flexible surface films that can accommodate the volume changes during periodic formation and decomposition of Si-Li alloys. We identified three ‘magic’ solutions, based on mono-fluorinated ethylene carbonate (FEC), 1-3 dioxolane (DOL) and ionic liquids with (FSO₂)₂N⁻ (FSI) anion and LiFSI for Si electrodes and discuss herein why they are so good. The same ionic liquids and DOL based solutions work very well with Li-S cathodes. We want to explain why. The chance to advance Li ion battery technology beyond its state-of-the-art depends on the ability to use high voltage cathodes (LiCoPO₄, LiMn₁.₅Ni₀.₅O₄ and Li & Mn rich layered transition metal oxides). What really determine the anodic limit of Li ion batteries? Do we have solvents with high enough intrinsic anodic stability? Maybe solutions based on ionic liquids. However, it is not clear that ILs are really relevant for practical batteries. We have to find electrolyte solutions in which effective passivation phenomena are developed on high voltage cathodes. It appears that FEC based electrolyte solutions develop protective surface films when polarized to high potentials. LiCoPO₄ cathodes can serve as a most suitable probe for testing electrolyte solutions which can develop appropriate passivating films at high voltages. The complications related to side reactions of electrolyte solutions are very severe with oxygen reduction processes. The oxygen reduction products (peroxide, superoxide) formed in the presence of Li ions are highly reactive with all kinds of polar-aprotic solvents. In too many studies of Li-oxygen systems, the importance of such side reactions is ignored. Another area that is being paid attention recently is non-aqueous Mg electrochemistry in connection to rechargeable batteries. We want to discuss in this presentation the simplest electrolyte solutions in which Mg electrodes can be reversible and the electrochemical window can be the widest possible. In summary, this presentation is aimed at discussing comprehensively the challenge of electrolyte solutions for next generation batteries and provide guidelines for further development.
HIGH VOLTAGE CATHODE MATERIALS FOR LITHIUM ION BATTERIES
- FROM MATERIALS TO COMPLETE CELLS -

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Dedicated to Prof. Robert Huggins on his 86th birthday

Long life, efficient and safe high energy storage systems are the key components for new car concepts (hybrid and full electric cars) as well as for intermediate storage of renewable energy sources. A very promising approach for further improvement of lithium-ion batteries is realizing new high-potential cathodes materials able to operate close to 5 V vs. Li/Li⁺. The application of these cathodes leads to a higher cell voltage, which leads to higher energy density, lower costs and a lower complexity of the complete battery system. In principle high voltage cathode materials like spinel type LiNi₀.₅Mn₁.₅O₄ or cobalt based olivines are well known for many years but still need to be further developed for practical applications with respect to cycling life in complete cells. The high charging potential of the cathode leads to increased electrolyte degradation and other side reactions with passive components like binder, current collector or separator that compromise the performance of the full cell. The SEI formation at the negative electrode is strongly influenced by electrolyte impurities formed by electrolyte oxidation on the cathode side. These side reactions can lead to capacity fading on the anode side and low cycling life in full cells. The presentation will give an overview about recent developments of high voltage cathode materials with respect to usable capacity, rate capability, cycling life and safety. Challenges for electrode design and processing for high energy cells and full cell development will be addressed. Performance and cycling data of a high energy 2 Ah stacked pouch cell containing a synthetic graphite anode and an optimized LiNi₀.₅Mn₁.₅O₄ cathode will be presented. Dominant ageing mechanisms and various approaches to overcome these problems will be discussed.
IMPROVED PERFORMANCE OF LITHIUM-SULFUR BATTERY WITH FLUORINATED ELECTROLYTE

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Despite the great promise, the Li-S battery poses several technological challenges, including fast capacity fading with cycling, high self-discharge rate, and low energy efficiency. Many of these issues are related to the internal “redox shuttle mechanism,” which results in parasitic reactions of dissolved lithium polysulfides (Li\textsubscript{2}S\textsubscript{x}, x=4-8) with the lithium anode and the loss of sulfur active material.\textsuperscript{[1]} A problem arises because of the dissolution of lithium polysulfide from the cathode into the electrolyte solvent—typically a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME).

In this paper, we present a new electrolyte containing an organo-fluorine compound, 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) for the first time for the lithium-sulfur battery. Fluoroether compound exhibits much higher hydrophobicity than its non-fluorinated counterpart, and as a result, its interaction with hydrophilic Li\textsubscript{2}S\textsubscript{x} is quite weak. A solubility test clearly indicated that Li\textsubscript{2}S\textsubscript{8} has very limited solubility in the mixture of Fluoroether 3 and DOL at a 1:1 or greater volume ratio, whereas it completely dissolves in the mixture of DOL/DME (1:1 ratio), a state-of-the-art (SOA) electrolyte for the Li-S battery (Fig. 1). The low solubility of lithium polysulfides in fluoroether solvent significantly affects their diffusion into the bulk electrolyte, mitigating the shuttle effect and enhancing the charging efficiency (Fig. 2).\textsuperscript{[2]} The new fluorinated electrolyte suppressed the deleterious shuttling effect and improved the capacity retention and coulombic efficiency in cell tests. In addition, it was found to eliminate the self-discharge of the lithium-sulfur battery.

\textbf{Fig.1.} Solubility test of Li\textsubscript{2}S\textsubscript{8} in solvents with and without fluorinated ether 3.  
\textbf{Fig.2.} Galvanostatic potential profiles of the 1\textsuperscript{st} charge and discharge profile of Li-S cell.

IN-SITU INVESTIGATION OF ATOMIC/MOLECULAR LAYER DEPOSITION COATINGS TOWARDS A BETTER UNDERSTANDING OF THEIR EFFECT ON ELECTROCHEMICAL PERFORMANCE

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Atomic/Molecular Layer Deposition (ALD, MLD) techniques have been applied to modify the surface of electrode materials in Lithium-ion batteries. The surface-modified electrodes exhibit significantly improved electrochemical performance, as demonstrated in our previous work.1,2 It is believed that these ultrathin ALD/MLD coatings protect the surface of an electrode from direct contact with electrolytes, and facilitate the formation of stable solid electrolyte interphases (SEI) different from the original SEI. In order to understand the effect of these ALD/MLD coatings on the electrochemistry of electrode materials, in-situ characterization has been successfully performed on the pristine and coated electrodes. For silicon (Si) anodes, in-situ Transmission Electron Microscopy (TEM) was applied to monitor morphology and chemistry evolution of both uncoated and MLD coated silicon nanoparticles. The results indicate the native silicon oxide has been converted to crystalline Li2O islands in the uncoated Si anode. The formation of Li2O essentially increases the impedance and irreversible capacity loss. On the contrary, MLD process has changed the surface chemistry of silicon, removed the native oxide and thereby mitigated the detrimental effects from the native oxide. This elastic MLD coating further accommodates the volumetric changes to enable highly reversible lithiation/delithiation. This presentation will present the results in detail and demonstrate the impact of coating on electrochemistry, morphology and structure of electrode materials.

Reference:
INVESTIGATING THE EFFECTS OF LiNO₃ AND IONIC LIQUIDS ON SEI LAYER FORMATION AND STABILITY IN Li-S BATTERIES.
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The lithium–sulfur (Li-S) battery is a potential candidate for the next generation of lithium batteries with a high theoretical specific energy of 2600 Wh kg⁻¹ (based on active materials only) and a high theoretical capacity of 1675 mA h g⁻¹, assuming complete reduction of elemental sulfur to Li₂S. However, this capacity is rarely achieved for more than a few cycles, mainly due to a host of reactions associated with the discharge products of sulfur (the polysulfides ‘PS’), which sets up a “redox shuttle” involving multistage redox reactions. The intermediate soluble discharge products, referred to as higher-order polysulfides, migrate to the anode and react with lithium, which leads to the corrosion/passivation of the anode, poor efficiency and short cycle-life. In addition, the final discharge products Li₂S and Li₂S₂ precipitate not only on the cathode surface, but also in the separator and in voids within the cell. This greatly lowers the rechargeability of the cell and effectively represents a loss of active mass [1, 2]. The electrolyte, as one of the main components of a battery, has a crucial impact on this behaviour. Ionic liquids (ILs) as room temperature molten salts have been considered as a new class of electrolyte materials for lithium-sulfur batteries in recent decades because of their wide potential electrochemical window, high chemical and electrochemical stability, low vapor pressure (consequently low flammability and negligible volatility), low solvation power toward ionic PSs compared to organic electrolytes due to weak Lewis acidic/basic nature which delays the onset of the mentioned shuttle effect [3, 4]. Another approach to suppress this shuttle effect is to modify the electrolyte with additives. It has been shown that LiNO₃ modifies the protective film on the Li anode (known as the solid electrolyte interphase, SEI), which can protect the Li anode from direct chemical reactions with PS [5]. We are studying the effect of LiNO₃ on the SEI layer in the Li-S system by using blended-ionic liquid electrolyte and comparing the results with those from equivalent cells with organic electrolytes. We find that the presence of LiNO₃ and IL in the electrolyte leads to higher initial capacity and better capacity retention (cycleability). We are investigating the surface chemistry of the anode with XPS, to gain a better understanding of how LiNO₃ and IL modify the SEI layer.

References:

Electrolytes are the key to the development of next generation of battery technologies. For lithium-ion batteries, there are a significant number of new cathode materials operating at a range of voltages beyond 4 V vs. Li|Li⁺. These materials present a range of challenges, including ensuring interfacial stability between the electrode and electrolyte material, high Li⁺ transport and ensuring that the electrolyte doesn’t cause current collector corrosion, to name a few. As a consequence, electrolyte formulations are complex solutions containing a range of solvents, salts and additives to ensure high performance and long cycle life of the device. The downside of this complexity is the long lead time in identifying mixtures or formulations that may address the multitude of battery requirements for use with specific electrode materials. In this presentation, we will introduce F.A.S.T.E.R – Fast Autonomous Screening Test for Electrochemical Response, a high throughput electrochemical screening technique developed at CSIRO to identify non-chromate corrosion inhibitors for metals. We are now adapting F.A.S.T.E.R. to allow us to both prepare and screen a multitude of electrolyte combinations and then, using intelligent algorithms based on input parameters provided by the user, identify potential formulations for further, deeper investigation. Further, F.A.S.T.E.R. can be applied with electrodes of any battery chemistry type to determine compatibilities with electrolyte formulations. F.A.S.T.E.R. offers a 24-7 approach to the identification and development of new electrolyte formulations, which will assist industry in speeding up the introduction of the next generation of lithium (ion) batteries.
Despite the great interest generated by neutrons’ sensitivity to lithium, in-situ neutron diffraction (ND) knew a slow development due to the intrinsic difficulties it held (1). We recently designed an electrochemical cell manufactured with a completely neutron-transparent (Ti,Zr) alloy (2), able to provide good electrochemical properties and ND patterns operando, with good statistics and no other Bragg peaks than those of the electrode material of interest. Importantly, this allows detailed structural determinations by Rietveld refinement during operation. The cell was validated using well-known battery materials such as LiFePO$_4$ and Li$_{1.1}$Mn$_{1.9}$O$_4$ (2) for real operando experiments conducted on the D20 high flux neutron powder diffractometer at ILL Grenoble, France. We report here in particular on a series of spinel materials Li$_{1+x}$Mn$_{2-x}$O$_4$ (x=0, 0.05, 0.1). The well-known difference in electrochemical performances (capacity fading) observed in this family of materials was thoroughly investigated using operando neutron diffraction. The study (3) showed that not only the volume change induced by the delithiation is reduced while going from LiMn$_2$O$_4$ to Li$_{1.10}$Mn$_{1.90}$O$_4$, but more importantly that the mechanism by which this happens is modified. In fact, while Li$_{1.10}$Mn$_{1.90}$O$_4$ reacts though a “simple” monophasic reaction (a solid solution), Li$_{1.05}$Mn$_{1.95}$O$_4$ shows the existence of a solid solution process followed by a biphasic reaction and LiMn$_2$O$_4$ even shows a sequence of two biphasic reactions. Both the above mentioned features contribute to make over-lithiated Li$_{1.10}$Mn$_{1.90}$O$_4$ a much better candidate for use in Li-ion batteries than the standard stoichiometric LiMn$_2$O$_4$. In more details, neutrons allow us to be sensitive to lithium’s atomic parameters, such as atomic coordinates and even site occupancy factors (SOFs), and thus to include them in our analysis by the Rietveld method to increase the accuracy of our time-dependent structural model. In the specific case of Li$_{1+x}$Mn$_{2-x}$O$_4$ spinels, this meant the possibility to correlate, for the first time, the evolution of lithium’s SOF with the electrochemical features of the materials, which is of key importance for understanding and therefore improving Li-ion battery materials. Moreover, the cell will be used for several in-situ experiments in late 2014, not only using standard neutron diffraction, but also to develop in-situ Neutron Pair Distribution Function analysis. The first results of these experiments will be reported.

References:
Innovative, unprecedented water-based production process, applied to both electrodes, minimizes environmental impact and reduces costs of cell manufacturing, while improving cell performances.

The innovative high quality materials used in anode, cathode and separator of Leclanché large-capacity LTO lithium-ion batteries provide very high mechanical and electrochemical stability during cycling and allow for tenths of thousands full-DoD cycles to be reached, even in highly demanding conditions (see Fig.1). The lifetime estimation exceeds 20,000 cycles and is little affected by C-rate.

In order to increase the energy density of LTO-based cells, Leclanché is developing high-voltage LNMO/LTO cells. The developed cells with water based electrodes show very good lifetime stability (see Fig.2), while gassing is still an issue.

Fig. 1: Lifetime characteristics at RT (21°C); influence of C-rate and lifetime estimation of 16 Ah cell

Fig. 2: Lifetime characteristics of 16 Ah (HV)-LNMO/LTO cell
There is a clear need to develop higher capacity lithium intercalation oxides with > 200 mAh/g practical capacity. I will show specific design guidelines on how higher capacity electrodes can be found. Today, nearly all high energy density cathodes for rechargeable lithium batteries are well-ordered materials where lithium and other cations occupy distinct sites, and disorder is generally interpreted as reducing the electrochemical performance. Through examples in layered oxides and in borates I will show how disorder can be used to achieve near theoretical capacity, though its introduction needs to be well understood and carefully designed for each specific crystal structure. In layered Li-oxides capacity is limited due to the rapid reduction of the c-lattice parameter at high state of charge which increases the activation energy for Li motion. Introducing Li-excess can create percolating channels of Li migration paths which are not sensitive to c-axis lattice parameter changes, thereby extending the range over which Li can be extracted. [1-2]. I demonstrate this in Li_{1.211}Mo_{0.467}Cr_{0.3}O_{2}, which achieves a capacity close to 300 mAh/g. In lithium-metal borates we have recently achieved the highest capacity in a poly-anion compound, and near theoretical capacity, by judiciously engineering Li mobility through selected anti-site disorder. Monoclinic borates have high safety and low poly-anion weight, but their one-dimensional diffusion channels block Li diffusion, at even small amounts of site disorder [3]. By creating compensating disorder which allows for inter-channel Li hopping we have created a borate cathode which achieves approximately 200 mAh/g, albeit at low rate.

3. J-C Kim et al., submitted
Na$_3$V$_2$(PO$_4$)$_2$F$_3$, A POSITIVE ELECTRODE MATERIAL OF HIGH INTEREST FOR NA-ION BATTERIES

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Although Li-ion is a technology of choice for portable applications and is now spreading to transport applications, concerns have been recently raised about the future availability and prize of lithium resources. Many alternatives are thus explored. As sodium is abundant and cheap and considering the knowledge reached on lithium’s intercalation chemistry the development of Na-ion batteries is expected to be fast. We focused our efforts on the vanadium polyanionic compound Na$_3$V$_2$(PO$_4$)$_2$F$_3$ that shows the reversible extraction of 2 Na$^+$ ions at an average voltage higher than 3.9 V vs. Na [1]. Na$_3$V$_2$(PO$_4$)$_2$F$_3$ was demonstrated to be extremely challenging from the synthesis and crystal structure point of view, since the whole family of compositions Na$_3$V$_2$O$_{2x}$(PO$_4$)$_2$F$_{3-2x}$ (0 ≤ x ≤ 1 with vanadium changing from V$^{3+}$ to vanadyle (VO)$^{2+}$) shows a phase diagram with a rich set of phase transformations depending on the composition and temperature [2-5]. Important discrepancies in the crystallographic unit-cell parameters are observed in literature for materials reported to be Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (x = 0), most of them being actually such as x > 0 with a partial oxygen substitution for fluorine. Until very recently the crystal structure of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ was described in the tetragonal space group P4$_2$/mmm. We revealed thanks to very high angular resolution synchrotron radiation diffraction that a small orthorhombic distortion exists [5]. That description in the Amam space group preserves the structural framework, but induces a different arrangement of the sodium ions, which is a key element to understand the behavior of electrode materials. Na$_3$V$_2$(PO$_4$)$_2$F$_3$ shows very attractive performances, that were first demonstrated in laboratory full cells [6] and more recently in 18650 Na-ion prototypes made at CEA-LITEN. Combining laboratory and synchrotron powder X-ray diffraction we observed for the first time an extremely complicated series of biphasic and solid solution reactions during Na$^+$ deintercalation from Na$_3$V$_2$(PO$_4$)$_2$F$_3$ [7], not detrimental to fast mobility of Na$^+$ ions in this framework.

This research was performed in the frame of the French network RS2E (http://www.energie-rs2e.com) and of the European network ALISTORE-ERI (http://www.alistore.eu). This project was partly funded by the French National Research Agency ANR (Descartes project SODIUM).

References
7. M. Bianchini et al. in preparation
HIGH-ENERGY CATHODE RESEARCH AT ARGONNE NATIONAL LABORATORY

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Lithium-metal-oxide chemistries have now been pushed very close to what may be their practical limit in terms of capacity and working voltage. Though considerable stores of lithium are present in LiMO₂ layered cathodes (M=Mn, Ni, Co), 30-40% of this lithium cannot be utilized in real cells due to instabilities involving both surface and bulk processes. Therefore, advances in lithium-ion cathodes will rely on the development of novel structural and elemental compositions as well as robust surface layers. These new designs require advanced characterization for a complete understanding of the complex, local- and long-range structures possessed by these materials; understanding that is necessary for insights into reaction and failure mechanisms. This presentation will focus on recent work at Argonne National Laboratory (USA) related to the design of next-generation, high-energy, cathode materials. Emphasis will be given to collaborations that have been established, across the laboratory and beyond, to take advantage of unique capabilities including powerful user facilities, such as the Advanced Photon Source, and a wide variety of scientific expertise.
The P2-Na$_x$(Fe,Mn)O$_2$ layered oxides in Na-Batteries

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In the perspective of the development at very large scale of renewable energy systems that require stationary batteries, the prevailing parameters are the lifetime, the price and the material availability. From these points of view, sodium based batteries have to be investigated. We studied Na$_x$(Fe,Mn)O$_2$ systems with a special focus on the electrochemical behaviour in relation with the oxygen packing of the starting material.

The study of the Na$_x$(Fe,Mn)O$_2$ systems for several Fe/Mn ratio leads either O3 to P2 type phases depending on the sodium amount and the on Fe/Mn Ratio. This presentation will be focused on the P2 type materials. Depending on the compositions either the Mn$^{3+}$/Mn$^{4+}$ or the Fe$^{3+}$/Fe$^{4+}$ redox couples can be involved. The participation of iron has been proved by ex situ and in situ XAS and Mossbauer spectroscopy.

The in situ XRD study upon intercalation shows the occurrence of orthorhombic distortions due to the Jahn-Teller effect of Mn$^{3+}$. The amount of this cation can be monitored either by the sodium intercalation or by the Fe:Mn ratio in the starting material. When almost all Na is deintercalated a new oxygen packing is reversibly formed.

A general overview of the properties of these materials will be presented.
FROM HALF CELLS TO FULL CELL

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High energy density, safe fast charging capability or long cycle-life are desirable features for most advanced batteries. Achieving satisfactory performance in all aspects requires extensive work at the material level together with optimized design of the full cell. Ideally, cell designers should be able to leverage available performance metrics available for both electrodes’ active materials (AM) from half cell testing in order to fine tune the properties of the full cell, even before the realization of the first prototype.

Throughout our previous work, we highlighted the role of two simple assembly parameters (see Fig. 1): first, the loading ratio (LR) which denotes the ratio between available capacities in negative and positive electrodes (resp. NE and PE), and second, the offset (OFS) which denotes the possible shift in terms of state-of-charge of both electrodes. Both these parameters can be used to describe the optimal use of both active materials toward achieving higher energy density, long cycle life and safe fast charging capability.

Here, we offer to explore some key relationships between properties (performance, degradation modes) of active materials in half cell setups and properties of the resulting full cell. Specifically, we will discuss the mathematical relationship between first cycle losses of both AM, formation of the passivation layers and the resulting OFS. We will also discuss the process through which the pre-formation LR can be optimized to yield maximum initial energy density and/or maximum cell longevity (cycle-life, calendar life).

![Fig. 1. Schematic of a full cell voltage curve based on NE and PE AM, LR and OFS](image)
Cubic variants of the garnet phase Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) are the subject of intense interest for battery applications because of their high ionic conductivities ($>10^{-4}$ S/cm) and apparent resistance to reduction by metallic lithium [1]. A number of obstacles have prevented successful utilization of LLZO as solid electrolytes in lithium batteries, including difficulties with densification, high reactivity with substrates, air, and moisture during processing, and large resistances at lithium interfaces. Our recent work has been directed towards understanding and overcoming these problems to enable development of high-energy batteries with metallic lithium anodes. To this end, we have successfully employed traditional low-cost ceramics processing techniques to lower the sintering temperature by 130° to 1100°C [2]. By manipulating the processing variables, we can fabricate dense samples of different thicknesses with various microstructures; large-grained, small-grained, and hybrid structures [3]. Spectroscopic experiments show that Li$_2$CO$_3$ forms on surfaces of dense pellets exposed to air for brief periods of time [4]. This can be responsible for the high interfacial impedances observed in cells. Li$_2$CO$_3$ layers as thin as a few nm result in greatly increased area-specific resistances (ASRs) in symmetrical cells containing LLZO solid electrolytes, but a simple polishing technique removes the Li$_2$CO$_3$ and reduces the ASR by nearly an order of magnitude. Furthermore, the microstructures of the dense LLZO pellets strongly influence the electrochemical properties. A symmetrical lithium cell containing a dense small-grained sample of LLZO prepared in our laboratory exhibited the lowest ASR (39 Ω-cm$^2$) ever reported for this material. The lower interfacial impedances associated with smaller grain sizes also result in more stable DC cycling at higher critical current densities for Li/LLZO/Li symmetrical cells. Reasons for the improved performance of the small-grained LLZO samples will be discussed further during the presentation.

TWO-POINT STATE-OF-CHARGE DETERMINATION IN LITHIUM-ION BATTERY PACKS
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The state-of-charge (SOC) estimation is of extreme importance for the reliability and safety of battery operation. How to estimate SOC for an assembly of cells in a battery pack remains a subject of great interest. Here a viable method for SOC determination and tracking for multi-cell assemblies is proposed and validated. Using 3S1P strings as an example, an inference of SOC is illustrated in a battery assembly based on a correct open pack voltage (OPV) versus SOC (i.e. OPV=f(SOC)) function. The proposed method only requires the measurement of the rest cell voltages of the single cells at two distinct occasions.

This new method offers great benefits to SOC calibration and tracking, which should improve the accuracy of any SOC tracking method (Figure 1). This method is not calculation intensive and could easily be implemented in any BMS. Additionally, we introduced two parameters which could be used to characterize and follow the imbalance evolution within a pack, and thus, enable RUL determination with improved accuracy.

Figure 1: Comparison between experimental data and simulation with and without the proposed method.

Coupled with our other diagnostics tools we believe that this approach could lead to a significant improvement of the quality of BMS SOC tracking and SOH diagnostics, for all applications where large battery assemblies are needed. As a matter of fact, and to the best of our knowledge, this is the first time where the pack-level (imbalance) and cell-level (aging) degradation factors of a battery pack could be distinguished and accurately quantified without any disassembly or maintenance downtime required.
Electrode/electrolyte interfaces have been extensively studied in Li-ion batteries. It is at the interface the electron transfer reactions occur, the lithium-solvated-ion becomes de-solvated and where surface compounds on the electrode can react with the electrolyte. New synchrotron-based techniques such as HAXPES (sometimes called tender XPS) where information can be obtained as a depth profile through the interface into the bulk of the electrode material by tuning the incoming photons has shed new and more details on the complex interface chemistry. High pressure photoelectron spectroscopy (HPXPS) can provide more realistic information about the sensitive solid-liquid interfaces when performing the experiments up to about 25 mbar.

In this presentation examples of some new studies of silicon exposed to liquid electrolytes and characterized with HPXPS will be described. By employing a new instrumentation developed in Uppsala [1,2] silicon exposed to PC and LiClO$_4$ has been studied. The presence of liquid electrolyte was achieved by designing a sample preparation and transfer procedure that allowed the introduction of electrochemical samples into the analysis chamber without an intermediate UHV step. It is demonstrated, that the solid /electrolyte interface can be considered stable well within the time frame to conduct thorough HPXPS analysis.

The HAXPES results will be illustrated by discussing the buried interface in graphite where the amount of lithium accumulating in the graphite surface can be quantified [3]. The implication of this result for the balancing of a full cell where graphite has been cycled vs. LiFePO$_4$ will be highlighted by also describing the interfacial reactions on the cathode [4]. The results will be compared to those of silicon where the interfacial chemistry in many ways is different due to the chemistry of the silicon oxide chemistry covering the silicon particles [5].

References
ABSTRACT

From the glove box to the garage—executing on the promise of next-generation lithium ion battery materials: the Applied Battery Research portfolio at the Office of Energy Efficiency and Renewable Energy

Realizing the promise of next-generation Li-ion batteries for EDVs is a central critical theme of President Obama’s EV-Everywhere Challenge. The initiative, which exists to make electric vehicles affordable, brings together the Office of Energy Efficiency and Renewable Energy’s Vehicle Technologies Office, the Office of Science’s Basic Energy Sciences Program, and the Advanced Research Projects Agency — Energy (ARPA-E). Affordable EDVs with all the functionality and performance of existing consumer products and the fulfillment of DOE’s energy security and environmental stewardship goals will create an enormous advanced manufacturing opportunity. US development of such durable and high performance electrochemical energy storage technologies will lead to American jobs.

Contrary to popular belief, the technical barrier to realizing an American revolution in manufacturing jobs is not the discovery of new materials or the invention of new energy storage devices, rather the barrier to commercial viability in the next decade is executing on existing next-generation materials and devices. Thus the overarching objective of the Applied Battery Research thrust within VTO is to translate discoveries made in U.S. universities and national labs into society-benefiting consumer goods—to move the technology form the glove box to the garage.

This talk will illustrate progress, opportunities, and barriers to this objective with recent results from portfolio projects underway at national laboratories, at corporate R&D facilities, and in academic labs. The presentation will conclude with an explanation of the program’s funding philosophy and goals, what is planned for future funding opportunities, and what is expected to be returned to the country through this investment.
ELECTROCHEMICAL STORAGE VIA REVERSIBLE METAL SULFIDE PRECIPITATION

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Solubilized sulfur electrodes offer an opportunity to capture nearly the theoretical capacity of the Li-S reaction through reversible precipitation when electrodes are designed to allow facile charge transfer, for example through the use of percolating nanoscale conductor networks. In this work we study the kinetics of reversible precipitation in two respects. Potentiostatic experiments show that precipitation of Li$_2$S on carbon follows Avrami kinetics corresponding to 2-dimensional nucleation and growth, supported by direct observations of precipitate morphology. This in turn suggests a mechanism whereby reduction of polysulfides occurs at the triple-phase boundary between conductive substrate, insulating precipitate, and solution phase. Second, dramatic solvent effects on rate are observed in the glyme family whereby the precipitation rate varies by nearly $10^4$ between diglyme and tetraglyme. Exchange current density measurements show similar variations between the same glymes, suggesting a common rate-limiting mechanism. Possible mechanisms for this behavior will be discussed.

Ionic Liquid Electrolytes for Sodium Battery Applications – A Study of the Effect of Concentration and Temperature on Sodium Transport and Electrochemical Behaviour.


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The enormous demands on available global lithium resources have raised concerns about the sustainability and cost effectiveness of lithium based energy storage. Sodium secondary batteries have emerged as promising alternatives to lithium batteries. We have recently explored the influence of Li concentration on ion dynamics and electrochemistry in a N-methyl-N-propylpyrrolidinium bis(fluorosulfonylimide) electrolyte [1] and here we describe an analogous study of sodium bis(trifluoromethylsulfonyl)amide (NaNTf₂) and sodium fluoro sulfonimidamide (NaFSI) electrolyte systems based on N-methyl-N-butyrypyrrolidinium bis(trifluoromethylsulfonyl)amide (C₄mpyrNTf₂) and C₃mpyrFSI ionic liquids. The electrochemical stability of the system was examined as a function of temperature and concentration with stable Na⁺/Na cycling evident at all temperatures and increased stability of a sodium metal symmetric cell at the highest sodium concentrations. NMR spectroscopy is used to investigate the ion dynamics in these systems and to correlate this with an apparently increased transport number at higher NaFSI content.

[1] H Yoon, PC Howlett, AS Best, M Forsyth, DR MacFarlane
The *tavorite* phase of lithium iron sulfate fluoride, LiFeSO₄F, exhibits a slightly higher redox potential than the commercialized LiFePO₄, based on the same transition metal. Due to a higher formula weight, the gravimetric capacity of the sulfate fluoride is lower but the energy density is comparable for cells based on these two cathode materials. The synthesis of LiFeSO₄F is in most cases proposed to include a topotactic reaction where water is extracted from iron sulfate monohydrate and substituted by lithium fluoride [1-3]. We have studied the synthesis by *in situ* X-ray diffraction using tetraethyleneglycole as the reaction medium, with different sets of precursors. The as synthesized material has low electronic conductivity and could thus benefit from a conductive coating of the particles. A conductive carbon coating is commonly achieved through pyrolysis of an organic precursor, e.g. sucrose. This process is not possible in this case, since LiFeSO₄F decomposes at a lower temperature than that required for the pyrolysis. We have chosen to use a conductive polymer coating, applied through a low temperature process. We have followed the coating process in some detail with electrochemistry, Mössbauer spectroscopy and microscopy. The successful polymer coating renders a material with a high capacity and low polarization when used in electrochemical cells. The electrochemical extraction and insertion of lithium is proposed to follow a two phase reaction involving the end members LiFeSO₄F and FeSO₄F. This proposition is based on X-ray diffraction results and the observation of a flat charge/discharge curve. Delithiation at low rate, however, reveals a small potential step of about 15 mV in the charge/discharge curve (Fig 1.), close to the composition Li₀.₅FeSO₄F. From X-ray diffraction and Mössbauer spectroscopy we have been able to propose a structure for this intermediate phase. The same phase can also be formed during lithiation of the material. This phase formation is not accompanied by any clear step in the charge/discharge curve.


Fig 1. Potential as a function of composition during delithiation and subsequent lithiation of LiₓFeSO₄F.
MULTI-DIRECTION OPTIMIZATION OF SI-BASED NEGATIVE ELECTRODES FOR LI-ION BATTERIES

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Silicon is a very promising alternative to the graphite anode, as it possesses a theoretical gravimetric capacity of 3579 mAh.g⁻¹ (mAh per g-Si), which is much higher than the 372 mAh.g⁻¹ of graphite. However, a large capacity fade is observed during cycling due to the large volume change of this material.  

Our strategy on Si-based negative electrodes is to focus on low cost synthesis routes and/or modification of cheap commercial samples. Our strategy is also to couple multi-characterization techniques to obtain deep comprehension of the reaction and failure mechanism, in order to optimize the performance and especially the cycle life.  

In this presentation, we review our recent strategies in order to improve the cyclability of low cost Si-based electrodes. We will show results on the first charge mechanism, the analysis of SEI composition and mechanism of SEI formation, the influence of pristine surface chemistry, the use of nanostructured and 3-D copper current collectors, and our development of ball-milled nanostructured Si-based electrodes.
The electrolyte is one of the key components of an energy storage device required to achieve, for example, high reliability and safety as well as high energy density. There are numerous battery chemistries possible, although lithium-ion has become one of the most common technologies for portable electronics and is making its way increasingly into electric vehicles and stationary storage.

We have found that pyrrolidinium and phosphonium ionic liquids based on TFSI and FSI give excellent performance for lithium batteries, particularly for electrolytes containing higher lithium salt concentrations.[1] These electrolytes offer attractive stable electrolyte properties and unique interfacial properties, key to the use of high energy density electrodes such as lithium metal. Likewise, plastic crystal materials are promising solid state electrolytes that can allow flexibility of design and can remove the safety risks associated with leakage and ignition of commonly used volatile liquid electrolytes. They can be classed as fast ion conductors, where one type of ion (i.e., Li⁺ for Lithium batteries) is able to move rapidly against a background of a relatively static matrix. Organic ionic plastic crystals (OIPCs) are an interesting type of plastic crystal, made entirely of ions, which have shown good performance as solid-state electrolytes in lithium batteries.

This presentation will describe our efforts to develop novel ionic liquid and OIPC polymer nanofibre composite electrolytes[1,2] and will highlight our advances in understanding and improving ionic transport and lithium redox performance for application in lithium metal based batteries.

References:
Prussian Blue Structure Materials With Rapid Kinetics and Long Cycle Life
For Grid Scale Energy Storage

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One of the major problems related to the integration of renewable energy sources with the large scale electric distribution grid has to do with short-term transients, which can occur with high frequency. The amelioration of this problem requires energy storage systems that can operate at very high rates, and with high efficiency over a very large number of cycles.

A group of inexpensive insertion reaction electrode materials with the open framework Prussian Blue crystal structure can be employed as very attractive electrodes in aqueous electrolyte electrochemical systems for this purpose. Experiments have already demonstrated the outstanding properties of some members of this family. Over 40,000 full cycles have been achieved at a very high (17C) rate, with a coulomb efficiency of 99.7%.

Information about the structural features of this group of materials that lead to these unusual properties, as well as the properties of several different compositions, will be presented.
NEW TITANIUM DIOXIDE HIGH POTENTIAL NEGATIVE ELECTRODES

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Toshiba Corp. pioneered in commercializing a new class of lithium-ion batteries with high cycleability, high rate-capability, and high safety, using spinel lithium-titanium oxide (Li$_5$Ti$_4$O$_{12}$, LTO) as a negative electrode. However, the use of LTO sacrifices significantly the energy density of the resulting batteries because of its high working potential (ca. 1.5 V) and a low theoretical capacity (175 mAh/g). We have proposed that two kinds of titanium dioxides, B-type and ramsdellite TiO$_2$ (Theo. Cap.: 335 mAh/g) are promising as alternative high potential negative electrodes. Here we overview the preparation methods and the charge-discharge properties of TiO$_2$(B) and ramsdellite TiO$_2$ (TiO$_2$(R)).

TiO$_2$(B) powder was prepared from K$_2$Ti$_4$O$_9$ or Cs$_2$Ti$_5$O$_{11}$ precursor[1-3] The alkali metal ions of the precursor was first ion-exchanged to protons in 1 M HCl, and then the protonated titanium oxide was dehydrated at 500°C for 30 min to obtain TiO$_2$(B). TiO$_2$(B) had a reversible capacity > 250 mAh/g at C/6 with a good cycleability (Fig. 1) [3]. However, the tap density of TiO$_2$(B) samples were low (~0.3 g/cm$^3$) owing to its needle-like shape (500 nm $\phi$ x 2 $\mu$m), which resulted in a low volumetric energy density. We made several attempts to control the shape and the size of TiO$_2$(B) by using Nb-doped TiO$_2$ powder with a large particle size (~20 $\mu$m) as a precursor material [4] and by milling the precursor material before the ion-exchange and dehydration processes [5] to improve the tap density.

LiTi$_2$O$_4$ powder was prepared from Li$_2$CO$_3$ and TiO$_2$ by firing at 1000°C in H$_2$/Ar atmosphere, and TiO$_2$(R) was obtained after acid leaching. TiO$_2$(R) has a reversible capacity of ca. 210 mAh/g at C/6 with a good cycleability (Fig.1). The discharge potential was low (ca. 1.5 V) up to SOC = 50%, but increased to ca. 2.0 V after SOC = 50%, which gives a lower energy density than TiO$_2$(B). TiO$_2$(R) showed a good rate-capability (Fig. 2), though the particle size was larger (~3-10 $\mu$m) than that of TiO$_2$(B).

Fig. 1. Charge and discharge curves of TiO$_2$(B) and TiO$_2$(R) at a C/6 rate in LiPF$_6$/EC+DEC(1:1) at 30°C.

Fig. 2. Rate-capability of TiO$_2$(B) and TiO$_2$(R) in LiPF$_6$/EC+DEC(1:1) at 30°C.

CONDUCTING POLYMER ADDITIVES FOR MILLIMETRIC THICK ELECTRODES OF LI BATTERIES

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One of the greatest challenges in the current research in lithium-based batteries is reaching the high energy values necessary for applications such as pure electrical vehicles at the minimum cost. The required scaling up of porous electrode thickness brings up however, severe restraints to the specific capacity obtained in practice due to limitations to electronic and ionic transport. To overcome these limitations we put forward the use of conducting polymer additives in porous electrodes, which are able to act as conducting fillers, and mechanical reinforcement materials. In the case of the low-cost conducting polymer polyaniline (PANI), the excellent properties of a completely deprotonated lithium-doped state PANI in terms of specific capacity, stability on cycling and rate capability are presented. The coating of bare LFP particles with thin layers of this new PANI allows clearly surpassing the performance of commercial carbon coated LFP electrodes [1]. The role of PANI and PEDOT conducting polymers additives into millimetric thick electrodes of NMC material will also be presented and discussed in light of electrochemical their responses.

Simulated amorphisation recrystallization methods, are now routinely used to generate models of various nano-architectures for metal oxides with complex microstructural details [1,2]. In the current studies the desired nanostructures of manganese dioxides, were produced from an amorphous nanoparticle. Lithium was inserted into various crystallised nanoarchitectures, up to a possible maximum quantity, and related lattice expansion was studied by simulated X-ray diffraction patterns and microstructures. Furthermore, corresponding voltage profiles of the various nanoarchitectures of manganese dioxide are estimated. Lastly, pressure induced changes in mechanical properties of different nano-architectures are analysed from radial distribution functions, microstructures and elastic moduli. Tunnels that provide a pathway for lithium in the nanoporous architecture are maintained at high pressures as compared to those of the bulk structure.

FIRST PRINCIPLES STUDY OF HIGH CAPACITY ELECTRODE/ELECTROCATALYST MATERIALS FOR HYBRID LITHIUM-ION/LITHIUM-OXYGEN CELLS

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Li-ion batteries suffer from low capacities while Li-O2 batteries have high overpotentials and hence low energy efficiency. Taking as inspiration Li$_5$FeO$_4$, which when used as an electrocatalyst in Li-O2 cells reduces overpotentials and demonstrates a high capacity unrelated to Li$_2$O$_2$ formation [1], we introduced the general concept of using lithium-metal-oxides with high Li$_2$O content as combination electrodes/electrocatalysts in hybrid Li-ion/Li-oxygen cells [2]. Using first principles density functional theory (DFT) calculations, we performed a high-throughput search for similar hybrid materials with high capacities and suitable properties [3].

While these materials exhibit promising capacities of up to 1000 mAh/g, their reaction mechanisms remain unknown. In this presentation, we will discuss DFT investigations of the reaction mechanisms in several of these materials, including Li$_5$FeO$_4$, Li$_6$MnO$_4$, and Li$_6$CoO$_4$. DFT calculations are performed to investigate the thermodynamics of Li and Li-O removal from these materials, in order to establish the details of the charge reaction. Atomistic and electronic structural changes in the materials are tracked during the reactions. Results on the energetics indicate a cross-over between pure lithium removal and concomitant oxygen loss, which is electronically shown to be correlated with development of the peroxide-like character of oxygen.

Acknowledgement
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References
CHEMICAL IMAGING OF INTERFACES AND INTERPHASES IN LI-ION ANODES

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Most Li-ion battery chemistries involve the creation or transformation of materials under non-equilibrium environments. Because these chemical energy storage systems operate beyond the thermodynamic stability limits of the electrolytes, reactions between electrodes and electrolyte result in the formation of new phases and interphases, which hinder further electrolyte decomposition and assure battery operation over the lifespan of the application.

The basic physico-chemical properties and long-term stability of these surface layers known as the solid electrolyte interphase (SEI) determine the performance and durability of the entire system. However, our understanding of how and why some materials function, and, equally importantly, why some materials with many ideal characteristics actually fail, is mainly rudimentary and empirical.

The requirements for long-term stability of Li-ion batteries are extremely stringent and necessitate control of the chemistry at a wide variety of temporal and structural length scales. The advent of femtosecond (fs) lasers and near-field optical methods during the past decades has led to the development of new advanced techniques for chemical analysis. This presentation provides an overview of novel methodologies, which exploit micro and nano-manipulation techniques and single crystal model electrodes to provide sufficient sample definition suitable for advanced far- and near-field Raman and FTIR, XAS, and pumped laser probes and electrochemical characterization techniques.

Examples of detailed in situ molecular characterization of Sn and Si electrode surface and bulk processes at the nano-level scale exceeding the diffraction limit will be discussed.

Acknowledgements
This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, under contract no. DE-AC02-05CH11231. This work was also supported in part by the Chemical Science Division, Office of Basic Energy Sciences, Office of Nuclear Nonproliferation, and the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.
Additives to Extend the Life of Lead Acid Batteries
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We have improved our organic polymer activator by using an acryl polymer. The acryl polymer provides far better lead-acid battery performance than our previous polymer (PVA=polyvinyl alcohol). The additive acts by improving the performance of the negative electrode lead acid battery. The vinyl polymer strongly adsorbs on the surface of the negative electrode and raises the hydrogen overvoltage (the side reaction of the negative electrode in lead-acid batteries).

This new polymer is very effective in significantly reducing sulfation and produces active lead from the large lead sulfate granules. We recommend 1 to 2 grams of the polymer added to each cell of a 12-volt lead-acid battery (40-150Ahr) and deep cycle forklift batteries. The cost is about $US4-6 every two years for a battery life extension of 8-10 years. We have also demonstrated that all SLI (starting, lighting, ignition) batteries can be reduced in size by more than 50% without reducing the battery life for trucks, buses, taxis, etc.

More than $40 billion worth of lead-acid batteries are produced per year around the world. About 65% of this production is for engine starting (SLI) batteries. The organic polymer activator improves the SLI battery life 2 to 3 times to 10-15 years. This will have a significant positive effect on our environment and energy savings.
HYBRID POLYSILSESQUIOXANE IONOGELELECTROLYTES FOR HIGHTEMPERATURE LITHIUM BATTERIES

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Hybrid ionogels fabricated with 1M LiTFSI in N-butyl-N-methylpyrrolidinium
bis(trifluoromethylsulfonyl)imide (BMPYTFSI) crosslinked with a ladder-like structured
poly(methacryloxypropyl)silsesquioxane (LPMASQ) were investigated as high temperature gel
polymer electrolytes for lithium ion batteries. In addition to the exceeding low crosslinker
concentration (~2 wt %) required to completely solidify the ionic liquids which allowed for high
ionic conductivities comparable to the liquid state ionic liquid (~0.5 mS/cm), these hybrid
ionogels exhibited superior thermal stabilities (> 400 °C). Lithium ion battery cells fabricated
with these gel polymer electrolytes at various C-rates at various temperatures showed almost same
cell performance as the cells with liquid electrolyte. Moreover, these hybrid ionogels exhibited
excellent cycling performance after 100 cycles at 90 °C, sustaining over 98 % coulombic
efficiency, while conventional organic crosslinking agents suffered from thermal degradation and
subsequent cell failure. Highly advantageous properties of these hybrid ionogels, such as high
ionic conductivity in the gel state, thermal stability, excellent C-rate performance, cyclability, and
nonflammability offer opportunities for applications as high temperature electrolytes.

Figure 1. Cyclability of HI-2 ionogel compared with a conventional organic ionogel fabricated
with ETPTA, with the inset figure showing the representative discharge profiles

Main text for the abstract should be in Times New Roman font, size 12, single-spaced, and
justified. Leave 1 inch to all sides as margin on Letter size paper. Citations should be listed in the
Hybrid Polysilsesquioxane Ionogel Electrolytes for High Temperature Lithium Batteries
The rapid growth of the integration of renewable energy sources such as wind and solar into power grids has spurred extensive research on the energy storage technologies that could improve grid reliability and utilization.\[1\]–\[3\] Electrochemical batteries including lithium-ion, high temperature sodium sulfur and lead acid batteries are amongst the currently deployed energy storage solutions for grid applications.\[4\] Each has its limitations, including high cost, poor safety and limited cycle life, respectively. Recently, aqueous metal-ion (specifically Li\(^+\) and Na\(^+\)) batteries are of great interest due to their safety and potentially lower cost.\[5\]–\[12\] Aqueous sodium-ion battery NaTi\(_2\)(PO\(_4\))\(_3\)/Na\(_4\)Mn\(_9\)O\(_{18}\) system show high-power capability and good high-rate cycling performance.\[11\] However, we also identified that the capacity fading is very serious at low current rates especially in the electrolytes with neutral pH and low salt concentrations, which leads to a very poor calendar life. This serious capacity fading at low rates is derived from side reactions between electrodes and H\(_2\)O and O\(_2\) in the aqueous electrolyte. In order to gain a fundamental understanding of the poor calendar life, a comprehensive investigation is conducted on factors (e.g., electrolyte pH and salt concentration) that influence the electrode stability in aqueous electrolyte. This study helps the battery community to better understand the issues and challenges of aqueous battery systems that are based on intercalation electrodes and could possibly provide solutions to further improve the calendar life.

Dilithium (2, 5-dilithium-oxy)-terephthalate (Li$_4$C$_8$H$_2$O$_6$) as a novel organic catalyst for Li-O$_2$ battery

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As an advanced large-scale energy storage and conversion system, the rechargeable non-aqueous Li-O$_2$ battery has recently attracted considerable attention because of its high gravimetric density since it was firstly presented in 1996 [1]. In an ideal Li-O$_2$ battery, on discharge, O$_2$ is reduced at the cathode, where it combines with Li$^+$ released from the Li-metal anode to yield Li$_2$O$_2$ (oxygen reduction reaction (ORR), 2 Li$^+$ + O$_2$↑ + 2 e$^-$ → Li$_2$O$_2$). On charge, Li$_2$O$_2$ is converted back to Li$^+$ and O$_2$ (oxygen evolution reaction (OER), Li$_2$O$_2$→2 Li$^+$ + O$_2$↑ + 2 e$^-$)) [2]. One of the critical challenges which limit the implementation of Li-O$_2$ batteries is the low round-trip efficiency and poor cyclability resulting from a large over-potential. Although the real effect of catalytic activity is controversial and the mechanism of catalyst is not yet clear, it has been widely accepted that the employment of catalyst can minimize the over-potential of Li-O$_2$ battery. Up to now, a number of materials have been employed as cathode catalysts, such as noble metal (alloy), carbon, transition-metal oxide, showing some improvement.

Herein, we present a noble organic catalyst-Dilithium (2, 5-dilithium-oxy)-terephthalate (Li$_4$C$_8$H$_2$O$_6$), which is expected to display an excellent electrocatalytic activity for OER. Its electrocatalytic performance was evaluated by tracking the decomposition of Li$_2$O$_2$ in a during the charge process in a Li-O$_2$ cell. The real time kinetics of OER was also investigated by synchrotron radiation powder X-ray diffraction (SR-PXD), which is a direct and effective diagnostic technique to study the degradation of Li$_2$O$_2$ throughout the charge process without any addition of artifacts from post treatments. In addition, the full cell displayed overpotential of 0.86 V in the first cycle and stable cycling performance for over 40 cycles.

Figure 1. Discharge/charge profiles of a Li-O$_2$ cell using Li$_4$C$_8$H$_2$O$_6$ as catalyst. Inset: Delivered capacities from discharge and charge vs. cycle numbers of the cell

REFERENCES

Both, batteries and foodstuffs are high performance energy storage systems. In this presentation, various common and uncommon features will be discussed.
HIGH-ENERGY, LONG-LIFE LITHIUM-SULFUR BATTERIES

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The current lithium-ion technology based on lithium-insertion compound electrodes is limited in energy, so cathodes like sulfur have become appealing as they offer an order of magnitude higher capacity and are abundant and environmentally benign. However, several challenges prevent the practical application of lithium-sulfur batteries: high resistivity of sulfur and the discharge product Li$_2$S, dissolution of the intermediate reaction products (polysulfides) into the electrolyte, shuttling of the polysulfides between the cathode and anode, and poisoning and degradation of the lithium-metal anode by the dissolved polysulfides. These difficulties result in low electrochemical utilization of sulfur and poor cycle life. Significant improvements have been made in recent years, but further improvements and a better understanding of the lithium-sulfur batteries are still needed.

To overcome the difficulties, this presentation will focus on the following strategies: (i) novel cell configurations with a microporous carbon paper interlayer between the cathode and the separator, (ii) carbon-coated bifunctional separators, (iii) carbon-dissolved polysulfide cathodes, (iv) in situ formed Li$_2$S-carbon cathodes, and (v) stabilized lithium-metal surface with additives. For example, the carbon-paper interlayer or the carbon-coated separator decreases the resistance of the sulfur electrode, facilitates the absorption of soluble polysulfide shuttling in the electrolyte, and acts as a second current collector for accommodating the migrating active material from the sulfur electrode. This novel approach not only simplifies the processing without requiring elaborate synthesis of composites and surface chemistry modification, but also improves the rate capability and cycle life with high sulfur content and loading. A variety of carbon interlayers have been developed for this approach, including binder-free carbon nanotube (CNT) paper, microporous carbon paper, and naturally abundant materials like carbonized eggshell membranes and plant leaves.

Li/dissolved polysulfide batteries utilize dissolved active material and enhance the kinetics of the redox reactions of sulfur. A variety of binder-free, free-standing carbon papers, including carbon nanotube (CNT) paper and carbon nanofiber paper, have been utilized as a current collector with polysulfides. Lithium metal or lithiated anodes are required to be used in lithium-sulfur batteries since the sulfur cathodes do not have any lithium in the initial stage, which poses a significant safety hazard. Use of Li$_2$S as a cathode can overcome this problem, but it is not straightforward to make the Li$_2$S cathode because of its high resistivity and reactivity in air. Our group has developed a simple Li$_2$S-CNT sandwiched electrode which can effectively trap the air-sensitive Li$_2$S in the electrode with good electron and ion accessibility. Also, another approach to chemically synthesize Li$_2$S in situ by using a lithiated graphite as a lithium donor to reduce polysulfides will be presented. Finally, the use of additives to form a robust, smooth lithium-metal surface in contact with polysulfides will be presented.
Li$_2$FeSiO$_4$ is considered a promising cathode material for the next-generation Li-ion battery systems owing to its high theoretical capacity, thermal stability and low cost [1]. Its key limitation is the poor rate performance ascribed to intrinsically slow Li$^+$ kinetics within this material at ambient temperature [2]. In this study, the rate performance of Li$_2$FeSiO$_4$ at high temperatures is investigated, and a comparison of the phase transition behavior observed between high- and room-temperature cycling is elucidated.

Two-electrode cells were used to conduct electrochemical measurements at 25$^\circ$C and 160$^\circ$C. Conventional organic electrolyte (i.e., LiClO$_4$) was used for electrochemical measurements done at 25$^\circ$C. Molten salt (ionic liquid) was used as electrolyte for measurements conducted at 160$^\circ$C. Synchrotron X-ray diffraction data of charged Li$_2$FeSiO$_4$ electrodes were collected at the beam line BL02B2 (SPring-8 (Japan)).

Initial cycling at 160$^\circ$C leads to a complete transformation from the monoclinic Li$_2$FeSiO$_4$ to a thermodynamically stable orthorhombic LiFeSiO$_4$, concomitant with the occurrence of significant Li/Fe antisite mixing. Initial cycling at 25$^\circ$C, however, leads to retention of the parent Li$_2$FeSiO$_4$ (with the monoclinic structure as a metastable phase) with little cationic mixing. Our results reveal that excellent rate performance with good capacity retention is attainable upon cycling of Li$_2$FeSiO$_4$ at high temperatures thanks to the faster phase transformation to the thermodynamically stable Li$_2$FeSiO$_4$ phases triggered by high temperature.


**Figure** Schematic comparison of the phase transformation occurring upon initial charging of Li$_2$FeSiO$_4$ to LiFeSiO$_4$ between 25$^\circ$C and 160$^\circ$C.
NEW INSIGHTS INTO LI-S BATTERIES:

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Li-S rechargeable batteries are still far from reaching the market place due to several limitations. Among them are: (i) the use of a Li metal anode with liquid electrolyte (ii) the insulating character of sulfur and the ending product Li\textsubscript{2}S and (iii) the soluble polysulphide species generated during the battery operation, which diffuses throughout the separator and deposits on the Li side resulting in a loss of active material.

Herein, we drastically deviate from confinement approach\textsuperscript{1,2} and use a liquid cathode obtained either by dissolving polysulphides within the electrolyte like a semi-redox flow battery or by placing sulphur powders in contact with the Li negative electrode. Such approaches are shown to result in greater performances than confinement approaches. By using in situ complementary techniques such as CV measurement\textsuperscript{3}, UV-vis experiment\textsuperscript{4} and impedance spectroscopy, we will monitor the amount and the evolution of the dissolved polysulfides in different electrolyte together with the formation of a SEI layer at the Li electrode.

A survey of different electrolyte additives\textsuperscript{2} able to trigger chemical reactions converting Li\textsubscript{2}S into soluble lithium polysulphides will be presented together with the polysulphide evolution upon cycling monitored by complementary \textit{in situ} techniques; the latter have already proven to be feasible either for quantitative analysis through CV measurement\textsuperscript{3} or identification of soluble species by UV-vis experiment\textsuperscript{4}.

References


DECIPHERING THE THERMAL BEHAVIOR OF LITHIUM RICH CATHODE MATERIAL FOR LITHIUM-ION BATTERIES BY SYNCHROTRON-BASED X-RAY TECHNIQUES

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Recently, composite layered material between Li2MnO3 and LMO2 (where M= Mn, Co, Ni), also known as the lithium rich cathode material, has received pronounced attention and has been considered as promising cathode materials due to their high discharge capacity of ~250 mAh g\(^{-1}\). However, there are several intrinsic problems associated with this material family that need to be solved; e.g., the voltage as well as the capacity decay during cycling, the high irreversible capacity loss in the first cycle, poor rate capability, and oxygen release during cycling, in order to adopt these materials in practical cells. Thermal stability is another challenge which could greatly impact the safety of lithium-ion batteries. However, it has received little attention unlike the widely studied electrochemical performance and reaction mechanism of this material. In this study, we use in situ X-ray diffraction technique to elucidate the thermal degradation mechanism of 0.5Li2MnO3-0.5LiNi0.33Co0.33Mn0.33O2 lithium rich cathode material in the absence and presence of electrolyte to simulate the real life battery conditions and compare its thermal behavior with the commercial LiNi0.33Co0.33Mn0.33O2 cathode material. We show that the thermal induced phase transformations in delithiated lithium rich cathode material are much more intense compared to similar single phase layered cathode material in the presence of electrolyte. The structural changes in both cathode materials with the temperature rise follow different trends in the absence and presence of electrolyte between 25-600 °C. Phase transitions are comparatively simple in the absence of electrolyte, the fully charged lithium rich cathode material demonstrates better thermal stability by maintaining its phase till 379 °C, and afterwards spinel structure is formed. In the presence of electrolyte, however, the spinel structure appears at 207 °C, subsequently it transforms to rock salt type cubic phase at 425 °C with additional metallic, metal fluoride, and metal carbonate phases.
Without a doubt the Holy Grail of battery research is the development of a post lithium ion technology. This may require a shift towards batteries containing a pure metal anode. Li metal is an attractive metal anode in part due to its high volumetric capacity (2062 mAh cm\(^{-3}\)), a high reductive potential of -3.0 V vs. NHE and the wide availability of lithium electrolytes. However, its deposition occurs unevenly with formation of dendrites which leads to safety concerns during cycling. In contrast to lithium metal, magnesium metal deposition is not plagued by dendritic formation. Additionally, magnesium is more stable than lithium when exposed to air, more abundant in the earth crust and provides a higher volumetric capacity (3832 mAh cm\(^{-3}\)). However, magnesium has a reductive potential of -2.36 V vs. NHE and has a unique electrochemistry which prohibited the use of magnesium analogues of lithium electrolytes. Since the oxidative stability of electrolytes governs the choice of cathodes it is of paramount importance to develop non-corrosive magnesium electrolyte with wide electrochemical windows which will permit discovery of high voltage cathodes. In this talk we will present the latest developments and future challenges which must be overcome.\(^{1,2,3,4,5}\)

S/PPY COMPOSITE CATHODES FOR LI-S BATTERIES PREPARED BY FACILE IN-SITU 2-STEP ELECTROPOLYMERISATION PROCESS

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In this work, a direct process for fabricating high capacity sulfur cathodes for Li-S batteries is described. This process obviates the need for the traditional sulfur cathode preparation methods using lengthy pasting and casting [1-3] and at the same time have better control over the physical and electrochemical properties of the final cathode. The process involves two electropolymerisation steps using polypyrrole conductive polymer with the first utilising a bulky polymeric dopant, such as Nafion, polystyrene sulfonate or polyacrylic acid and the second involving a low molecular weight inorganic or organic dopant such as lithium sulphate or p-toluene sulfonate. Besides sulfur, carbon black was added to the electropolymerisation mixture to enhance the dispersion of sulfur and to improve the electrical conductivity of the final product. The process of cathode preparation can take up to 3 hrs and can be scaled up to suit larger cathodes requirements with dimensions around 100 cm² for pouch cell preparation. Two types of flexible conductive substrates were used in this work; fine stainless steel mesh and carbon cloth fabric. The prepared cathodes were characterised by SEM and revealed highly porous structure and uniform coating compared to cathodes prepared by single step electropolymerisation. Sulfur loading in these cathodes varied from 5% to 40% based on the amount charge consumed during the electropolymerisation process where higher loadings were obtained upon consuming low charges. Coin and pouch cells were prepared using these cathodes and showed high capacity (~ 1000 mAh/g), efficiency (> 97%) and good capacity retention after 50 cycles at a C/10 rate.

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Comprehensive Understanding of Battery Safety

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As lithium-ion battery technologies mature, the size and energy of these systems continues to increase (> 50 kWh for EVs and MW for utility storage). This increase in energy density and complexity of these systems makes safety and reliability of these high energy systems increasingly important. While most materials advances for lithium-ion chemistries are directed toward improving cell performance (capacity, energy, cycle life, etc.) and cost, there are a variety of materials that can be utilized to improve lithium-ion battery safety; which also translates to actual costs and performance over the lifetime of the system. Issues including energetic thermal runaway, electrolyte decomposition and flammability, anode SEI stability, and cell-level abuse tolerance continue to be critical safety concerns. At the battery and system scale, physical hazards (fire or explosion) are generally only evaluated in the general public consideration of relative safety. However, potential health hazards and environmental impact should also be considered to form a comprehensive view of system safety (which is of particular concerns for large grid-tied systems). Experimental testing techniques, analytical characterization, modeling, and advanced diagnostics/prognostics are all tools that can be used to develop a complete understanding of abuse tolerance and safety issues. This presentation highlights our work and the work of others in the community to develop a comprehensive understanding of lithium-ion battery safety from the materials- to the system-level scale.
RECENT DEVELOPMENT OF MAGNESIUM RECHARGEABLE BATTERY USING POLYANION COMPOUND CATHODE AND INORGANIC ELECTROLYTE

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Magnesium rechargeable batteries are one of interesting candidate for next generation battery system. The advantages of magnesium metal anodes have been previously recognized[1, 2], and a magnesium rechargeable battery cell was first proposed in 2000[3]. However, the energy density remained rather constrained by the cathode material, and the narrow potential window, corrosion, and safety problems posed by the electrolyte have hampered the commercial realization of these batteries. Even though extensive research has been performed[4], the cathode materials await breakthroughs for the development of practically usable rechargeable magnesium batteries. In this study, we address the problems plagued by the cathode materials by using concept of ion-exchanged polyanion cathode, MgFeSiO₄ and demonstrate a rechargeable magnesium battery using this high energy density cathode material[5].

The preparation of MgFeSiO₄ involves, two electrochemical processes, namely, 2Li⁺ extraction from Li₂FeSiO₄ followed by Mg²⁺ insertion. The charge-discharge profiles in a magnesium battery cell of the electrochemically prepared MgFeSiO₄ are shown in Fig. 1. The application of ion-exchanged MgFeSiO₄ polyanion compounds as magnesium rechargeable battery cathode materials enables a capacity of more than 300 mAh·g⁻¹ at an average potential of 2.4 V vs. Mg²⁺/Mg, with good retention upon cycling. The electronic and crystal structure changes upon charging and discharging process, which demonstrates the (de) insertion of magnesium in the host structure.

We propose a novel magnesium battery system where ion-exchanged MgFeSiO₄ and Mg metal are used as the cathode and anode, respectively, and Mg(TFSI)₂-triglyme as the electrolyte. These materials would be highly beneficial for increasing the energy density of the electrode materials in magnesium batteries without imposing significant constraints on available resources.

References:
NEW PROPOSAL ON DIAGNOSTIC METHODS FOR COMMERCIAL LITHIUM-ION BATTERIES THROUGH ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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EIS (Electrochemical Impedance Spectroscopy) has been utilized to characterize each factor of batteries, because it enables us to analyze dynamics of each elemental step sensitively and separately without destruction of the cell. In addition, non-destructive EIS is expected to utilize for premonitory diagnosis of batteries on board in electric vehicles. In our previous study, the equivalent circuit to express each elemental step in a commercial lithium ion battery (LIB) by EIS has been carefully investigated [1-3]. Finally we proposed the designed equivalent circuit (Fig. 1), and on the equivalent circuit, the impedance responses of LIB during capacity fading were analyzed with continuous charge-discharge cycling.

In the case of the higher LIB capacity, the internal resistance would shift to low (shown in Fig. 2). Ordinary EIS using conventional frequency response analyzer (FRA) – potentiostat systems is not easy because of its low internal resistance. Thus, we propose on the power controller of LIB system to create a signal for analyzing the battery health. Application of square wave for input signals of EIS was investigated in commercial LIBs to verify a new technique called “Square-current electrochemical impedance spectroscopy (SC-EIS)” which is a method for EIS without using the FRA systems. At the presentation, detailed explanation of these analyses will be introduced and discussed on their potential for reliable analysis of impedance spectra.

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Fig. 1 A) Typical Nyquist plots and, B) a proposed equivalent circuit of commercial LIB. [1-3] Dots show the results of calculation by equivalent circuit. Open symbols show the results of EIS.

Fig. 2 Relationship between the capacity of commercial LIBs and their internal resistance.
TITANATES AND RELATED MATERIALS AS NEGATIVE ELECTRODES FOR SODIUM-ION BATTERIES: $A_2Ti_6O_{13}$ AND TiO$_2$ HOLLANDITE

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Sodium ion batteries are coming back to the focus of research for large scale stationary electrical storage owing to sustainability, lower cost and worldwide resources. Comparable to lithium ion battery electrode materials, a wide portfolio of candidates needs to be investigated before a sodium-ion battery reaches commercialization. There are many positive electrode materials that are now presently being assessed while only few negative ones have been reported so far. Though Na and Li are very similar some of their differences (coordination preferences, ionic potential, etc.) are extremely important and fully determines electrochemical performances; therefore, an effort to understand better of crystal chemistry of sodium intercalated compounds should be done. We have recently studied the electrochemical behavior of a set of homologous titanates, $A_2Ti_6O_{13}$ ($A=$H, Li or Na) as well as the hollandite polymorph of TiO$_2$ (TiO$_2$(H)). A close relationship of the electrochemical behavior with the different crystal chemistry of Li and Na has been observed. Thus the site position of A in the $A_2Ti_6O_{13}$ ($A=$H, Li or Na) structure explains the different mechanism of the lithium intercalation reaction$^{1,2}$ as well as the limited capacity of $A_2Ti_6O_{13}$ upon sodium intercalation. A very recent and interesting example of the differences in performances is the case of TiO$_2$ (H) in which the amount of intercalated Na is approximately half of that observed in the case of lithium due to coordination preferences of guest ions.$^3,4$

Increasing demand of high energy density and high capacity batteries require development beyond Li-ion technology, such as multivalent batteries, and innovations in electrodes and electrolytes, alike. Rechargeable energy storage based on multivalent chemistry is likely to be cheaper than Li, and can also theoretically provide at least twice the energy density as compared to traditional Li-ion batteries. However, development and commercialization of multivalent batteries is critically dependent on the development of novel electrolytes with wide electrochemical windows and good conductivity, and that are compatible with both electrode materials, specifically the metal anode, as conventional electrolytes fail to penetrate the metal passivation layer.

In this work, we present *ab initio* calculations coupled with classical molecular dynamics simulations for potential magnesium salts in various solvents. We present structure, dynamics, energetics and stability analysis of potential magnesium salts in seven commonly used solvents, to obtain trends and information across chemistry and structure. We observe strong ionic association of the Mg$^{2+}$-anion pair across most solvents. These results have obvious implications for charge transfer and conductivity, however we also find that that such ionic association significantly affects the stability of the anion at reducing potentials. This information provides critical predictive capability about the stability of electrolytes depending on ionic association of salt. Additionally, the MD simulations show that solvation structure and diffusion coefficient changes significantly with anion and solvating species. Comparing the results to similar studies available for Li-ion systems, we find that the inter-molecular solvation structure for multivalent ions is very different from well-performing monovalent ion (e.g. Li and Na) electrolytes and hence points to a design metric for future electrolyte work.
The Ellingham diagram stands out as one of the most recognized graphs in the field of materials engineering. Yet the original diagram published by Ellingham 70 years ago [1] remains a mystery. This talk explores the origins of the diagram and the relationship between the Gibbs energy plotted on the left axis and the nomographic scales on the right, and proposes a few subtle changes for improved accuracy and utility.

Solid-solid interfaces are the key to enable high-performance solid-state batteries. The charge transfer at the barrier between electrode and electrolyte needs to be highly efficient in order to allow significant power to be drawn from solid-state devices. In this work, we have investigated the behavior of the high-voltage cathode material LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) in contact with various ceramic coatings (crystalline conducting, crystalline blocking, amorphous). Thick films of LNMO were prepared by a sol-gel method on Au substrates, and subsequently coated with Li$_4$Ti$_5$O$_{12}$ (LTO), ZrO$_2$ (ZrO), and LiNbO$_3$ (LNO), respectively. Electrochemical cells of the type Au/LNMO/coating/LP30/Li were built and characterized.

Electrochemical impedance showed that the charge transfer resistances at the interfaces LNMO/LTO and LNMO/LNO are similar to the charge transfer resistance at a pristine LNMO / LP30 interface, while the capacity retention is considerably improved by the LTO and LNO coating (Fig. 1). In comparison, the LNMO/ZrO charge transfer resistance is considerably higher.

TOF-SIMS investigations revealed that the interfaces were sharp, with little interdiffusion between the electrode and the coating.

This contribution will feature the detailed analysis of the interfacial layers at the solid-solid interfaces.

**Figure 1**: Charge-transfer resistance (left) and capacity retention (right) of a pristine LNMO / LP30 interface in comparison to LNMO/coating interfaces.
Carbon nanostructured materials are widely used in different energy applications: fuel cells, supercapacitors, Li-ion batteries etc [1, 2]. Several synthetic approaches can be used for preparation of CNTs, graphene etc, such as: CVD, exfoliation and other. Herein we report the adopted sacrificial support method (SSM) developed at UNM group [3-4] as a powerful tool for synthesis of materials for energy applications. Several types of 3D structured graphene materials were synthesized by modified SSM. The morphology control was achieved by variation of silica types, graphene oxide to silica ratio etc. After successful synthesis of graphenes the sacrificial support was leached by means of concentrated HF. Figure 1a represents SEM image of 3D structured graphene synthesized by SSM.

**Figure 1:** SEM image of 3D structured graphene.

TEM analysis confirmed the formation of multi-stacks of graphene layers (Fig. 1b). As synthesized 3D graphene can be used as matrix for encapsulation of nanosized silicon particles. The pores and voids in the carbonaceous material will allow Si nanoparticles expand during the charge cycle. The SSM was also successfully used for synthesis of cathode materials for LiB applications. Different oxides with controlled morphology were synthesized and characterized by XRD, SEM, TEM and XPS methods.

Electrochemical energy storage devices in the form of batteries are ubiquitous in society, used in everything from children’s toys to mobile electronic devices, providing portable power solutions. There is a continuous drive for the improvement of batteries. A large proportion of the function of batteries arises from the electrodes, and these are in turn mediated by the atomic-scale perturbations or changes in the crystal structure during an electrochemical process (e.g. battery use). Therefore, a method to both understand battery function and improve their performance is to probe the crystal structure evolution in situ while an electrochemical process is occurring inside a battery.

Our work has utilized the benefits of in situ neutron diffraction (e.g. sensitivity towards lithium) to literally track the time-resolved evolution of lithium in cathode materials used in rechargeable lithium-ion batteries (Figure 1). With this knowledge we have been able to directly relate electrochemical properties such as capacity and differences in charge/discharge to the content and distribution of lithium in the cathode crystal structure. In addition, the ability to test smaller samples (e.g. in coin cells) with in situ X-ray diffraction has allowed us to probe other batteries types, such as primary lithium and ambient temperature rechargeable sodium-ion batteries.

In situ experiments that probe the time-resolved structural evolution during charge/discharge provide unparalleled insight into how electrodes evolve. Using this information a comprehensive atomic-scale picture of battery functionality can be created and permutations can be made to the electrodes that optimize battery performance. This talk will showcase some of our recent results on electrode structural evolution with respect to electrochemistry in fully functioning batteries.

Figure 1. The (left) battery used for in situ neutron diffraction studies on Wombat, high-intensity powder diffractometer at ANSTO. A (middle) selected reflection of the cathode (dark red) evolving as a function of time, correlated to the charge and discharge process in the battery. Snapshots (right) of the cathode crystal structure at various potentials during charge. Lithium is shown in green with shading indicating lithium occupancy and MnO₆ octahedra are purple. The discharged and charged state show only one lithium crystallographic position while during charge there are two lithium positions.
Effect of Fast Charging on Lithium-Ion Cells: Performance and Post-test Results

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As acceptance of electrified vehicles increases, the consumer would start to expect characteristics in the electrified vehicle similar to what they were accustomed to in an internal-combustion-driven one. Among these characteristics is the ability to refuel in a short amount of time. For an internal-combustion-driven car, this takes on the order of 5 to 10 min.

In its battery test manual for electric vehicles [1], the USABC+ established a test to determine the capability of a battery to accept charge at high charging rates to determine its efficiency and other effects of fast charging. In this test, the battery is charged quickly to return about 40% of its state of charge. As an example, the test would be used to charge a battery from 40% to 80% state of charge in 15 min. However, the high charge rates used may degrade the performance of the battery and, possibly, physically damage it.

We cycled commercially-available, cells containing two different chemistries using charge rates in the range of 0.7 to 6 C. The SOC returned was either 100% or 40%. The discharge rate was C/1 or C/3. Figs. 1A and 1B show the effect of charging at the 4C with SOC returned.

Fig. 1. Physical damage to the anode as a result of changing the SOC returned, A=100%; B=40%. The charge rate in both was 4C. B displayed more physical damage.

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The DOE Office of Electricity’s – Energy Storage program at Pacific Northwest National Laboratory (PNNL) has been focused on the development of cost effective energy storage technologies to improve the grid reliability, power quality, and adoption of the intermittent renewable energy. Among the most promising large-scale energy storage technologies are redox flow batteries (RFBs). RFB’s are electrochemical devices capable of storing up to multi-megawatt-hours (MWhs) of electrical energy via a reversible electrochemical energy conversion. Unlike traditional batteries in which the electrodes serve as the supply/sink of ionic charge, RFB’s store electricity in liquid electrolytes that flow on either side of a membrane. As such, the power and energy of a RFB can be separately designed, offering greater flexibility for a greater selection of stationary applications.

All-vanadium RFB system enlists the same element, vanadium, in both the catholyte and anolyte. Researchers at PNNL have revisited the standard vanadium sulfate electrolyte chemistry used in this system and developed an novel mixed acid electrolyte (sulfate and chloride) that can stabilize all four vanadium cations at concentrations ≥ 2.5M within a temperature range of 5~50°C. Recently, PNNL recently demonstrated a kW/kWh scale prototype battery utilizing this electrolyte system in order to better understand the system benefits of the mixed acid electrolyte. The system consisted of ~ 20 cell stack with 780cm² of active area/cell, ~ 30 liter electrolyte tanks, pumps and associated piping. The stack incorporated new interdigitated flow fields for reduced pressure drop and thinner Nafion membranes for improved performance. Results of stack testing under a wide range of current densities and temperature conditions will be reported along with resulting energy efficiencies.
DESIGNING SURFACE AND INTERFACE OF ELECTRODES
FOR LI ION BATTERIES

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The poor cell lifetimes of Li-ion batteries are rooted mainly in side reactions occurring at the electrode-electrolyte interface. The use of surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. This talk will include two parts:

In the first part, I will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries [1,2] including synthesis of coating materials such as Al₂O₃, ZrO₂, TiO₂, AlPO₄ and LiTaO₃ [3,4] as well as the ALD coating materials to modify the anode (Li₄Ti₅O₁₂, SnO₂) [5] and the cathode (commercial LiCoO₂, NMC) [6].

In the second part, I will discuss carbon coating on LiFePO₄ surface [7]. In particular, the focus will be on size-dependent surface phase change of lithium ion phosphate during carbon coating.

Reference:
Electrical Energy Storage: Looking back – looking forward

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This presentation will be a personal reflection of 40 years in battery research. Differences between government- and private sector supported research will be emphasized. Highlights of successes, stumbling blocks and failures will be described and a prognosis for a future breakthrough technology offered.
It has been an exciting year for grid energy storage applications. Battery companies, software companies, and utilities have accelerated the push to deploy electrochemical energy storage for grid applications. Southern California Edison has announced the largest energy storage project in North America. Tesla Motors announced its Gigafactory, with the intent to enter the grid market on both sides of the meter. And emerging companies are filling the need for new energy storage control software that integrates with existing grid software.

This overview presentation will review the big picture trends that are driving the increased use of electrochemical energy storage on the grid, along with the latest lessons learned from a 120Kw/500kWh storage unit tested for applications that include wind integration, demand response, and solar integration.
A higher energy and power of a lithium ion battery can be achieved with cathode materials operating at a higher voltage. 

LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{z}O\textsubscript{2} (NMC, with \(x + y + z = 1\)) with its most prominent protagonist LiNi\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} ("1/3-NMC") is regarded as one of the most competitive cathode materials due to the combination of decent capacity, lesser thermal and electrochemical instability in the charged state and lower cost compared to the well-known LiCoO\textsubscript{2}. Using 4.3 V vs. Li/Li\textsuperscript{+} as upper cut-off potential, 1/3-NMC delivers a specific charge of ca. 150 mAh g\textsuperscript{-1} (at low C-rates) and shows stable cycling performance at an average discharge potential of 3.86 V vs. Li/Li\textsuperscript{+} (= ca. 3.7 V cell voltage vs. graphite). With increasing the cut-off potential from 4.3 to 4.6 V vs. Li/Li\textsuperscript{+}, almost linear growth of the specific charge of ca. 190 mAh g\textsuperscript{-1} at a slightly higher potential of 3.95 V vs. Li/Li\textsuperscript{+} can be obtained.

However, cycling at 4.6 V vs. Li/Li\textsuperscript{+} inevitably results in a rapid capacity decay. Various failure mechanisms have been discussed in literature so far, including: oxidative decomposition of the conventional carbonate/LiPF\textsubscript{6} electrolyte, increase of the overall battery impedance, increased transition metal dissolution of the active material in the electrolyte due to manganese disproportional reaction and acidic attack by HF, oxygen release from the host structure, or irreversible phase changes.

In order to solve the problems associated with instabilities at the cathode/electrolyte interface, two approaches are intensively discussed in literature. On the one hand, there is the design of an electrolyte, which is thermodynamically stable vs. oxidation at the operation potential of the cathode. On the other hand, the addition of small amounts of film-forming electrolyte additives or the application of surface coatings and modifications of the cathode/electrolyte interface, lead to kinetic stability. Here we report on novel approaches for new classes of electrolyte additives improving the cycling stability of 1/3 NMC (used as model material for other high voltage cathode materials) at elevated cathode potentials, i.e., metal cation additives and novel HF scavengers.

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ADVANCED REDOX FLOW BATTERY TECHNOLOGIES

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This presentation describes the recent progress of the advanced redox flow battery technologies including both aqueous and non-aqueous systems. On the component level, new developments on the high energy density electrolyte, high selective membrane, and catalytic electrode will be reported. Novel high energy density redox flow battery systems including the Zn-I and Li-TEMPO RFBs combined with their NMR and Raman based solvation chemistry study will be discussed. Development of high selective membranes will be reported. Performance of the nanoparticles modified graphite felt electrode will be presented.
TESTING AND PERFORMANCE OF A NEXT GENERATION OF AQUEOUS HYBRID ION BATTERY FOR LARGE FORMAT STATIONARY ENERGY STORAGE DEVICE

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This presentation will cover the testing and the recent product performance improvements due to enhance electrolyte of large-scale energy storage electrochemical batteries. The core devices, which we are calling Aqueous Hybrid Ion (AHI) batteries, use a configuration wherein the anode consists of a composite system of activated carbon and NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, and the cathode is an MnO\textsubscript{2} – based alkali intercalation compound (typically cubic spinel \(\lambda\)-MnO). Both laboratory and field test data will be presented showing that large scale industrially packaged individual batteries with over 50 Ah in capacity and 300 Wh in energy have been produced, qualified, and inserted into large format systems.

Performance of next-generation AHI battery using high Na\textsubscript{2}SO\textsubscript{4}/Li\textsubscript{2}SO\textsubscript{4} concentration in aqueous electrolyte (approaching a total cation loading of 3 M) will be shown. Significant improvements in battery-level rate capability are observed without adding more active material in the system or changing its current collector architecture. Extended laboratory tests under various cycle and calendar life conditions will also be covered emphasizing how robust and safe this chemistry is in the face of common Pb-acid or Li-ion abuse tests.

Further data will show that packs of these batteries in the multi-kWh range have been effectively implemented in field-testing. This will include support for both smaller off-grid applications with bus voltages in the in the 20 to 100 V range, as well as, grid compatible systems with bus voltages in excess of 800 V as controlled by several different off the shelf inverter systems using custom battery management firmware. These data are especially compelling because no cell-level battery management system was used to maintain string integrity. The recombinant nature of the battery chemistry provides for a self-regulating overcharge condition that allows for even very high voltage battery strings to have long-term stability.

Key topics to be addressed include: (1) a description of the product performance improvements thanks to enhance electrolyte, (2) lifetime performance of this system in a range of cycle and calendar environmental conditions, (3) data from third party field tests in relevant applications showing the performance of our batteries under application specific load profiles, and (4) details on commercial microgrid projects that have been deployed at several off-grid locations.
To substantially increase the energy storage capabilities of lithium batteries it will be necessary to have more than one electron involved per redox center. One approach is to use magnesium as the anode. An alternative is to intercalate two lithium ions. In this latter approach the present commercial anode and electrolyte can be used. The cathode options will be discussed with an emphasis on vanadyl phosphate, which exists in a number of polymorphs and where the compounds LiVOPO$_4$ and Li$_2$VOPO$_4$ are known but not yet well understood. This research is supported by the DOE-EFRC-NECCES at Binghamton.

Robert A. Huggins Session
Some Introductory Comments
NECCES, Binghamton University, Binghamton, NY 13902-6000

Oxford University provided a stream of postdocs to Bob Huggins at Stanford. I was the second and saw the transition of Bob’s group to fast ion transport and battery materials. I will give an overview of that period.
MECHANICALLY ROBUST AND HIGHLY ION-CONDUCTIVE POLYMER-BLEND ARTIFICIAL SEI FOR HIGH-POWER AND LONG-LIFE LITHIUM-ION BATTERY ANODES

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The properties of the interface between electrode active materials and electrolyte are known to have profound effects on the performance of Li-ion batteries (LIBs). A large amount of research has so far been devoted to modifying the surfaces of active materials in order to enhance the overall performance of the electrodes. Majority of the research has resorted to inorganic oxide coatings, presumably due to their chemical stability, and different beneficial effects have been claimed for both cathode and anode materials. Relatively far less progress has been reported for polymeric coating. Compared with the inorganic ones, polymeric coatings typically require much lower processing temperature, and when used water as solvent, can be considered as more environmentally-friendly alternative. But most importantly, the rich chemistry of the polymeric coating intrinsically possess a greater flexibility for dealing with wide varieties of active materials and electrolytes for maximum performance.

In this presentation, we will report a new concept for forming an artificial solid-electrolyte-interphase (A-SEI) for Li-ion battery electrodes based on the rational design of multifunctional polymer blend to achieve favorable solid/electrolyte interfacial properties. Self-assembly between polymeric molecules as well as between polymers and the active material surface is enabled through interactions of specifically designed functional groups. It leads to the successful development of mechanically robust and highly ion-conductive binary polymeric electrode coatings with tailored functional groups for remarkably enhanced performance for graphite and graphite-Si composite anodes.

Figure 1. Remarkable enhancement in de-lithiation rate by polymeric blend SEI
Lithium-ions Migration in Li$_4$Ti$_5$O$_{12}$ Studied by Using in-situ Neutron Powder Diffraction

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In situ neutron powder diffraction (NPD) was used to study the migration of Li$^+$ ions in Li$_4$Ti$_5$O$_{12}$ anodes with different particle sizes during battery cycling and to reveal the mechanism of the increased capacity of the battery made with an anode of smaller particles. The lattice parameter, Li$^+$ ions distribution, and oxidation state of the Ti atom were monitored. The results suggest an increase in the rate of Li$^+$ ions incorporation into the anode rather than a change in the migration pathway as a result of the particle size reduction. The lattice of these anodes during continuous lithiation undergoes expansion followed by a gradual contraction and then expansion again. The measured lattice parameter changes were reconciled with Li$^+$ ions occupation at specific sites within the Li$_4$Ti$_5$O$_{12}$ crystal structure, where Li$^+$ ions migrate from the 8$\alpha$ to 16$c$ sites. Despite these similar Li$^+$ ions diffusion pathways, in larger-particle-sized Li$_4$Ti$_5$O$_{12}$ the population of Li$^+$ ions at the 16$c$ site is accompanied by Li$^+$ ions depopulation from the 8$\alpha$ site, which is in contrast to that observed in smaller-particle-sized anode where the results suggest that Li$^+$ ions at the 8$\alpha$ site is replenished faster than the rate of transfer of Li$^+$ ions to the 16$c$ site. Fourier-difference nuclear density maps of both anodes suggest that 32$e$ sites are involved in the diffusion pathway of Li$^+$ ions. NPD is shown to be an excellent tool for the study of electrode materials for Li-ion batteries, particularly when it is used to probe real-time crystallographic changes of the materials in an operating battery during charge/discharge cycling.
MULTIVALENT ION BATTERY CHEMISTRY: NEW RECHARGEABLE ZINC ION AND NICKEL ION BATTERIES

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Our society seeks the safety, environmentally friendly, and low cost batteries to meet the demand of the “next generation” electric or electrical devices. More recently, we have firstly proposed a storage mechanism of multivalent ion as a new strategy for energy storage, in which multivalent ions (Ni$^{2+}$, Zn$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, or La$^{3+}$) rather than conventional H$^+$, Li$^+$, Na$^+$, or K$^+$ ions are used as medium for energy storage[1]. This is a new strategy providing possibility for invention of new safety and ecofriendly energy devices based on various multivalent ions as shown in Figure 1. In this presentation, we will introduce two bran-new rechargeable zinc ion and nickel ion batteries invented by us[2].

A battery generally composes of a cathode, an anode, an electrolyte and a separator. The battery has to utilize battery chemistry, known as cathodic and anodic reactions occurring at the interface between the electrodes and electrolyte, to store energy. There are only several kinds of secondary batteries in the world, for example lithium ion, sodium sulfur, nickel metal hybrid, nickel cadmium, and lead-acid batteries[3]. Secondary battery is rare on crown in battery industries because it is difficult to gather two electrochemically reversible cathodic and anodic reactions in one electrolyte as the battery chemistry. At first we will introduce the multivalent ion storage mechanism and discuss the kinetics of charge process by using univalent and multivalent ions. Second, we will show the three steps to discover the battery chemistry. As examples, selected multivalent ions are used to discover energetic chemistry leading to invention of new green batteries. At last we will further demonstrate the advantages of these secondary batteries.

Reference

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Lithium Dendrite Suppression for Rechargeable Lithium Batteries

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Rechargeable Li-metal batteries are considered as one of the most important energy storage systems because Li metal anode has a significantly high theoretical capacity of 3860 mAh/g and the lowest electrochemical potential at -3.040 V vs. standard hydrogen electrode. However, the development and application of rechargeable Li-metal batteries has been hindered in the past four decades due to two major issues—the Li dendrite growth on Li anode during repeated charge/discharge processes leading to serious safety hazards and the low Coulombic efficiency since Li metal is strongly reactive to organic solvents and salt anions. During the last four decades, several approaches have been reported to improve the stability of Li metal anode, including using Li alloy, adding electrolyte additives, modifying Li surface, and so on. In many cases, the low Coulombic efficiency can be compensated by using excess Li (normally three times) in the batteries. However, the suppression on Li dendrite growth as far is not satisfactory.

In this work, we systematically investigated the effects of CsPF$_6$ additive and pre-formed surface film on Li deposition morphologies as well as the evolution of both surface and cross-sectional morphologies of the Li films during repeated deposition/stripping processes. It is the first time to report the growth of dendrite-free Li films with self-aligned and highly-compacted nanorod structure when Li was deposited in 1M LiPF$_6$ in propylene carbonate with 0.05 M CsPF$_6$ as additive. The formation of the compact Li nanorod structure is directly related to the pre-formed SEI layer on substrate and Li surfaces when deposited Li grows from isolated nucleation sites. Electrochemical analysis indicates that an initial reduction process occurs at ~2.0 V vs. Li/Li$^+$ before Li deposition, which is associated with the smooth Li deposition morphology. The XPS results indicate that the CsPF$_6$ additive can increase the LiF concentration in the film formed on the Cu substrate prior to Li deposition. In contrast, only a small amount of LiF appears in the film formed on Cu substrate prior to Li deposition for the CsPF$_6$-free control electrolyte. A fundamental understanding on the composition, internal structure and evolution of Li metal films may lead to new approaches to stabilize the long-term cycling stability of Li metal and other metal anode for energy storage applications. Details of the investigations will be reported and discussed in the presentation.

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Modulation of the interfacial properties of electrode with functional electrolyte additives for Li-ion batteries

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Li-ion batteries have been recently widely used in many commercial/industrial application fields, i.e. portable electronics (smart 3G/4G) mobile phones and power batteries for automobile applications etc. However, the electrochemical performance of the batteries are still far from a satisfied state in energy density, cycle life and safety. In order to achieve a higher energy density, longer cycle life and good safety, different strategies to further enhance their electrochemical performance have been designed and utilized. Among of them, controlling and monitoring of interfacial properties of a defined electrode systems in the full batteries by different additives are efficient ways to achieve the final targets.

In this presentation, a review of recent progress of high-voltage electrolyte will be given and some recent results of new recipes of electrolytes with different functional additives carried in this lab will be reported. We will show that cyclic performance of the positive electrodes in high voltage range or cyclic stability at high temperature and safety performance of the electrodes can be improved efficiently. The possible intermediates formed and reaction mechanism of the additives have been analyzed and proposed. It seems that an interfacial reaction not only affect the formation and growth of surface film, but also results in a high coulombic efficiency of the electrochemical reactions and finally the cyclic life and thermal stability of the batteries.

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Using Synchrotron Based X-ray Diffraction and Absorption and TXM to Study the New Electrode Materials for Next Generation of Batteries

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In developing high energy density cathode materials, layer structured Li$_2$MoO$_3$ is a very interesting model compound to study. In this presentation, we report the structural studies and charge compensation of Li$_2$MoO$_3$ during the initial charge and discharge. The close to fully reversible structural changes and Mo ion migration, originated from the charge compensation of Mo ions in both the Mo-O and Mo-Mo covalent bonds in the Mo$_3$O$_{13}$ cluster, make Li$_2$MoO$_3$ an appropriate alternative of Li$_2$MnO$_3$ in constructing new xLi$_2$MoO$_3$·(1-x)LiM$_2$O$_3$ cathode materials, which may have less lattice-breathing range and oxygen evolution during cycling.

Recently, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, denoted as LNMO, has attracted a lot of research attention as a promising high-energy density cathode material based on its higher operating voltage at ~4.7V vs. Li+/Li compared to the parent material, LiMn$_2$O$_4$. On the other hand, the poor cycle and calendar life of LNMO, especially at elevated temperatures, still remain one of the major challenges in its widespread applications. Extensive research has addressed some key factors determining its capacity and rate performance, such as cation ordering, transition metal substitution, and the Li-insertion/extraction mechanism. A combination of in situ synchrotron time-resolved x-ray diffraction (TR-XRD) coupled with mass spectroscopy (MS) and in situ x-ray absorption spectroscopy (XAS) during heating, as well as transmission x-ray microscopy (TXM) were applied to study the thermal stability of this material. The effects of Fe doping on capacity and thermal stability were also studied.

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HQ R&D on Silicon Anode for High Energy Li-ion batteries: Nano vs Micron

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In situ and ex situ scanning electron microscopy of nano, micro Si and SiO anode particles was carried out during the first cycles, and at various stages of charge. The particle size effects were explored in the range 0.1–20 μm, providing a new insight into the micro-structural evolution of the particles as a function of their size, and into the ‘mechanical’ resistance upon important volume change upon phase transformation of these anodes. For small particles, the failure of the battery comes from an electrochemical sintering that compacts the whole electrode, which results in its cracking. The particles keep their integrity when the discharge is stopped at a voltage 0.1 V, which corresponds to the chemical composition Li\textsubscript{12}Si\textsubscript{7}, while the particles are known to crack at deeper discharge up to Li\textsubscript{22}Si\textsubscript{5}. Replacing the Si particles by SiO particles in an attempt to avoid these structural effects did not help, because of the different chemical reactions during cycling, with the loss of oxygen. New process of Silicon from ingot to nano size will be presented.