ALD for Fuel Cells & Lithium Ion Batteries

Publication Review on Savannah and Fiji Systems
Highlights

- Fully optimized recipes (wafer scale) for Li (Li$_2$O), Mn, Co, Ni, Fe, P binary oxides
- Multicomponent oxide recipe available for cathode and electrolyte
- Carbon-free Li$_2$O (<0.1%) chemistry
- First ever reported quaternary oxide (LiFePO$_4$)
- Demonstrated multicomponent Li oxide in 300:1 aspect ratio (Expo mode)
- Glovebox integration for Savannah and Fiji
- In-situ QCM to characterize composition of multicomponent oxides
- Low Vapor Pressure Delivery (LVPD) available for wafer-scale uniformity and run-to-run reproducibility
- Most published Li-based work on Ultratech tools
Lithium ion battery

- Slow Li ion motion in and out of storage electrode
- Long transport path for electrons and ions
- Insufficient interfacial surface
- Extra weight (binder, separator, electrolyte)
- Battery degradation over time
- Safety concerns

Benefits of 3D microbatteries

• Higher power density due to short diffusion path
• Higher charge/discharge rates from higher surface/volume ratio
• Improved cycle life due to minimization of mech. stress and ALD passivation
• Active ion storage materials for electrodes (anode and cathode)
• Safe and not flammable: Solid Electrolyte

Huge potential for MEMS due to small form factor, low weight, high energy density
Li$_2$O / MnO$_x$ / Li$_2$MnO$_4$

- Depositions at low precursor temperatures to limit thermal decomposition
- In-situ characterization of process space for LiOtBu and Mn(EtCp)$_2$ chemistries with water and ozone
- Saturation curves
- Dehydroxylation of LiOtBu/H$_2$O films
- Optimized deposition of Li$_2$O and MnO$_x$ nanolaminates films
- Determined conditions for growth of MnO$_x$ on lithium based oxides.
- Controlled stoichiometry via Li$_2$O: MnO$_x$ cycle ratio
- SIMS confirmed QCM-based Li:Mn ratio and low % contamination
Real-time, in-situ sensing
Spectroscopic ellipsometry
Downstream mass spec

ALD (thermal, plasma, ozone)
MnO₂, Al₂O₃, TiO₂, TiN, AlN, & combinations

ALD Nanostructure Lab UMD

Surface analysis
Kratos Ultra DLD
Mono-XPS, mapping/imaging (3-15μ)
SEM, scanning Auger (100-200nm)
Depth profiling (Ar, coronene)
UPS, ISS
Carbon free Li$_2$O

- Depositions in Fiji F200 with LiOtBu, H$_2$O and O$_2$ gas (PEALD)
- In-situ characterization with XPS
- LiOtBu / H$_2$O
  - LiOH at $T < 240^\circ$C
  - Li$_2$O at $T > 240^\circ$C
  - Carbon-free Li$_2$O
- LiOtBu / P$_{O_2}$ lead to Li$_2$CO$_3$
- Carbon contamination from CO$_2$ via insitu XPS study
- Insitu ellipsometry study of LiOH dehydration vs temp.

Lithium Tantalate Solid-state Electrolyte

Objectives
- Solid-state electrolyte for 3D microbattery
- Li ion conductivity (1E-5 – 1E-8 S/cm), low electron conductivity

Experimental
- Savannah S100 at 225°C, expo mode
- LiOtBu @170°C, Ta(OEt)5 (190°C) / H2O
- Final Aspect Ratio ~ 470


2E-8 S/cm Li+ conductivity in Li$_{5.1}$TaO$_z$ at 299K

Conformal deposition of Li$_{5.1}$TaO$_z$ in 300:1 AAO
LiPON Solid Electrolyte


- **Experimental**
  - FIJI F200 at 250°C
  - LiOtBu @165°C / H₂O /
    Trimethylphosphate / N₂ plasma
  - Deposited on carbon nanotube sponge scaffold

- **Results**
  - First reported LiPON ALD process
  - 1.45E-7 S/cm highest published conductivity by ALD
  - Low %C <1%

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**Sequence for LiPON ALD using TMP**

**Stoichiometry / crystallinity vs %N**

**Ionic conductivity vs. %N**

**CV for LiPON on Si and Cu**

- **Experimental**
  - FIJI F200 at 250°C
  - LiOtBu @165°C / H₂O /
  - Trimethylphosphate / N₂ plasma
  - Deposited on carbon nanotube sponge scaffold

- **Results**
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LiFePO$_4$ cathode

Objectives

- First quaternary oxide for battery reported
- Cathode materials for Li-ion battery
- High specific capacity, low cost, thermal stability, environmentally friendly
- Improve rate performance via nanostructuring

Experimental

- Savannah S100 at 300°C, expo mode
- Ferrocene FeCp$_2$ (130°C) /O$_3$, Trimethylphosphate TMPO (75°C) / H$_2$O and LiOtBu (180°C) / H$_2$O
- Deposited on Si and CNT

Conformal LiFePO$_4$ on carbon nanotubes

Battery performances using LiFePO$_4$ electrolyte
FePO₄ on LiNi₀.₅Mn₁.₅O₄ cathode

- **Achievement**
  - Ultrathin FePO₄ on LNMO powder
  - Electrochemically active barrier between electrolyte and LNMO
  - Improves capacity fading and LNMO capacity

- **Experimental**
  - FePO₄ at 300°C, Savannah S100 (FeCp₂/O₃, TMPO/H₂O)


FESEM & HRTEM of LMNO with 20 cy. FePO₄

Impact of n-cycles FePO₄ on LMNO electrochem. pp.
Cu$_2$S cathode for LIB

Cu$_2$S on SWCNT (100, 200, 400, 600 cycles)

Charge/discharge for first 3 cycles at 1000 mA/g


- **Objectives**
  - Cu$_2$S deposited on single wall carbon nanotubes

- **Experimental**
  - Savannah S200 at 135°C, expo mode
  - CuAMD (150°C) and 1% H$_2$S
  - SWCNT functionalized with 9min O$_3$

- **Results**
  - Core-shell SWCNT-n-Cu$_2$S exhibits high charge discharge/stability
  - high capacity (260mA/g)
  - >99% Coulombic efficiency
Xiao, B. *et al.* Unravelling the Role of Electrochemically Active FePO4 Coating by Atomic Layer Deposition for Increased High-Voltage Stability of LiNi0.5Mn1.5O4 Cathode Material. *Advanced Science* n/a–n/a (2015). doi:10.1002/advs.201500022


FUEL CELL
Y$_2$O$_3$ and YSZ

- **Experimental**
  - Savannah S200 at 200-350°C
  - Y(EtCp)$_2$ @120°C (LVPD) / TDMAZr / H$_2$O

- **Results**
  - 0.8Å/cycle GPC @ 220°C, 2.1 index, 0.8%
    Uniformity on 200mm
  - QCM metrology shows good growth of Y$_2$O$_3$
    on ZrO$_2$
  - Composition control by ratio of
    Y$_2$O$_3$ : ZrO$_2$ cycles
  - RBS characterization
    - Composition in agreement with ALD ratio and QCM data
    - Carbon contamination not detected
  - XPS and XRD characterization under way

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QCM response during YSZ growth

GPC & index of Y$_2$O$_3$ vs temp.