The Materials Genome ...

... and the example of polymer dielectrics design

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The “Original” Genome

“The molecular logic of the living state”

Knowledge: Structure ⇔ Function Relationship

The Genetic Code
A Framework For Learning

Chemical & Physical Space → Experiments Computations → Property Space → Databases → "Rules" Mining → Knowledge & Discovery

Learning, Prediction & Search

The Materials Genome Challenges: Handle staggering chemical (~100 elements) and physical (3-d, multi-scale) spaces!
The ABX$_3$ Genome


A, B : 52 metals

X$_3$ : O$_3$, O$_2$N, ON$_2$, N$_3$, O$_2$S, O$_2$F, OFN

~ 19,000 possibilities

20 Candidates identified (out of ~19,000 cases)
Rules for stable ABO$_3$ insulators:
1. Even number of electrons per unit cell
2. Sum of oxidation states zero
3. A-site element larger than B-site element

Do we need to do ~ 19,000 DFT calculations to identify 20?!

Evolutionary algorithm appears to work
A Framework For Learning

Chemical & Physical Space

Computations

Property Space

“Rules” Mining

Valence, oxidation state and size rules

Stability, band gap and edges

Databases

Learning, Prediction & Search

Knowledge & Discovery

CMR

GA

Chemical space exploration for fixed structural template (cubic ABX₃)
# Materials That Rocked The World!

<table>
<thead>
<tr>
<th>~ 2000 BC</th>
<th>~ 400 BC</th>
<th>~ 300 BC</th>
<th>~ 1855 AD</th>
<th>Steel industry considered an indicator of economic progress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hittites develop iron weaponry</td>
<td>Wootz (ூட்டு) steel made in South India, Srilanka</td>
<td>Steel makes it to Damascus</td>
<td>Steel made by Bessemer process</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>~ 100 AD</th>
<th>~ 800 AD</th>
<th>~ 1100 AD</th>
<th>~ 1400 AD</th>
<th>~ 2020 AD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsai Lun invents paper</td>
<td>Paper made in Samarkhand &amp; Baghdad</td>
<td>Paper making arrives in Europe</td>
<td>Gutenberg revolutionizes printing</td>
<td>Paper made obsolete by iPad &amp; Kindle!!</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>~ 1855 AD</th>
<th>~ 1920 AD</th>
<th>~ 1976</th>
<th>~ 2000 AD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel made by Bessemer process</td>
<td>Staudinger discovers polymerization</td>
<td>The polymer/plastics industry outstrips steel</td>
<td>Polymers enter electronics/energy</td>
</tr>
</tbody>
</table>

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<tr>
<th>Mayans (2000 BC to 250 AD)</th>
<th>1839 AD</th>
<th>1920 AD</th>
<th>1976</th>
</tr>
</thead>
<tbody>
<tr>
<td>play with rubber balls!</td>
<td>Goodyear discovers vulcanization</td>
<td>Staudinger discovers polymerization</td>
<td>The polymer/plastics industry outstrips steel</td>
</tr>
</tbody>
</table>

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<tr>
<th>~ 1945-1947</th>
<th>1957 AD</th>
<th>~ 1960s AD</th>
<th>1965 AD</th>
<th>~ 2000s AD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transistor by Bardeen, Brittain, Shockley</td>
<td>Fairchild Semiconductor</td>
<td>Moore’s Law!</td>
<td>Intel is born</td>
<td>“High-k” dielectrics</td>
</tr>
</tbody>
</table>

**Iron & Steel**

**Paper**

**Polymers**

**Silicon**
The “Materials” Genome Initiative

- Not just high-throughput computing/experiments (i.e., data generation)
- Not just database creation (i.e., data organization)
- Not just data mining
- All the above ...
- … plus synergy between experiment, computation & theory, aimed at accelerated materials discovery

“The Materials Genome Initiative, the interplay of experiment, theory and computation”, de Pablo, Jones, Kovacs, Ozolins and Ramirez, Current Opinion in Solid State and Materials Science (2014)
The Polymer Genome
Capacitors are the only option for rapid (dis)charge applications.

Maximum energy density $\approx (\text{dielectric constant}) \cdot (\text{breakdown field})^2$
Capacitor Options

- Ceramics (planar & multilayer), but breakdown is catastrophic
- Polymer films
  - Preferred for large area applications
  - Display graceful failure

Toyota Prius Capacitor Bank
Medical Defibrillators
The Current “Standard”

- Biaxially oriented polypropylene (BOPP)
  - Purely hydrocarbon based
  - Large breakdown field (700 MV/m); Low loss (0.0001);
    Cheap; Easily processable
  - But, low dielectric constant (2.2)
  - Energy density of 5 J/cc

- How to surpass BOPP?
Our “MGI” Effort & Team

- Search the organic & organometallic chemical space …
- … for materials with
  - High dielectric constant
  - High breakdown field (large band gap?)
  - Low loss (large band gap?)
  - High temperature stability
  - Easy processability

Rational Design of Advanced Polymeric Capacitor Films
www.ims.uconn.edu/MURI

Multidisciplinary University Research Initiative (MURI)
The Length Scale Challenge

DFT computations, effective medium theory, 3-D structure searches (evolutionary algorithms, minima hopping, melt-and-quench, force fields), data mining, machine learning

Our Strategy

“Rational Design of All-Organic Polymer Dielectrics”, Sharma, et al, accepted (Nature Communications)
Organic Polymers

High-throughput density functional theory

Blocks: CH₂, CO, CS, O, NH, C₆H₄, C₄H₂S

- Electronic part of dielectric constant is strongly related to band gap; but ionic part is not!
- “Sweet spot” dominated by NH, CO or CS, and at least one aromatic group

3D Structure Prediction

Constrained evolutionary search (based on DFT energies)

NH-CO-NH-C₆H₄

Melt-and-quench based search (based on force-fields)

Courtesy: Artem Oganov (SUNY, Stony Brook)

Courtesy: Sanat Kumar (Columbia University)
3D Structure & Properties

NH-CO-NH-C₆H₄
(polyurea)

CO-NH-CO-C₆H₄
(polyimide)

NH-CS-NH-C₆H₄
(polythiourea)

But none of them is “processable”, i.e., flexible thin films cannot be made!
A Processable Variant

[-NH-CS-NH-C₆H₄-NH-CS-NH-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-]ₙ

Synthesized Film

Predicted Structure

XRD

IR

Dielectric

Breakdown

Courtesy: Greg Sotzing, Yang Cao (UCONN)
The Story So Far

Step 1: Combinatorial Chemical Space Exploration
Polymer block options: -CH₂-, -C₆H₄-, -C₆H₃S-, -CO-, -NH-, -O-, -CS-

Step 2: Promising Repeat Unit Identification
High-throughput density functional theory (DFT)
Effective medium theory

Step 3: Structure/Morphology Predictions
Evolutionary structure search (based on DFT)
Melt-and-quench based search (based on force-fields)

Step 4: Property Predictions
Dielectric tensor (using perturbation theory), Band structure (using hybrid functional), Infrared and x-ray spectra

Step 5: Synthesis, Testing & Validation
Solvent casting of polymer films
Infrared and x-ray spectra, Dielectric spectroscopy

“Rational Design of All-Organic Polymer Dielectrics”, Sharma, et al, accepted (Nature Communications)
Can We Do Better?!

Coordination chemistry across Group 14 hydrides and halides!

TYPE- A
CH₂, CCl₄, CF₃, SiH₄,
SiCl₄, SiF₄, GeH₂, SnH₂,
PbH₂,
CN = 4

TYPE- B
GeF₄, GeCl₂
CN = 5

TYPE- C
SnF₂,
CN = 6

TYPE- D
SnCl₄, PbCl₂
CN = 6/7

TYPE- E
PbF₂,
CN = 8

... by ushering in Group 14 elements?

Property variation across Group 14 hydrides and halides!

HSE Band Gaps (eV)

Electronic Dielectric Constant

Ionic Dielectric Constant

Polymers Based on Group 14 Elements

High-throughput density functional theory + Machine Learning

Blocks: CH$_2$, SiF$_2$, GeF$_2$, SnF$_2$, SiCl$_2$, GeCl$_2$, SnCl$_2$


Based on number of singles, doubles and triples

Prediction By Machine Learning

Correlations & Insights

- Ionic part dominates dielectric constant
- Sn-containing groups occupy “sweet spot”

Synergy With Synthesis

Ramprasad Group

How about Sn-esters?
Ge too expensive
How about Sn?

Sotzing Group

Make this:
$(CH_2)_x(GeF_2)_y$

Oh yeah,
$(CH_2)_x(SnCl_2)_y$ is magical! Can you make this?
Organo-tin Ester Polymers

The whole series via minima hopping!

Baldwin, et al (under review)
Deeper into Organo-tin

Tran, et al (in preparation)
Deeper into Organo-tin

\[(\text{SnF}_2)_x(\text{CH}_2)_y \text{ and } (\text{SnCl}_2)_x(\text{CH}_2)_y\]

- Structures determined using the minima-hopping method
- 1D, 2D & 3D motifs, with 4-7 fold coordinated Sn

Organic Versus Organo-tin Polymers

• By carefully choosing organic blocks, one can improve upon polypropylene

• Organometallic polymers could lead us to an important part of the chemical/property space!

• But, there are other issues to contend with, of course!
“New perspective on formation energies and energy levels of point defects in non-metals”,
Dielectric Breakdown: A New Frontier?! 

- The intrinsic breakdown field of a crystalline material is controlled by the scattering of charge carriers by phonons.
- How about extrinsic factors?!

"The intrinsic electrical breakdown strength of insulators from first principles" 
Kim, et al (in preparation)
A Framework For Learning

The Materials Genome Challenges: Handle chemical and physical spaces; accurate property prediction scheme development; synergize with experiments.
Acknowledgments

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