New-Generation Cathodes and Anodes: Understanding What Information in Reports Determine Viability to Enter Marketplace

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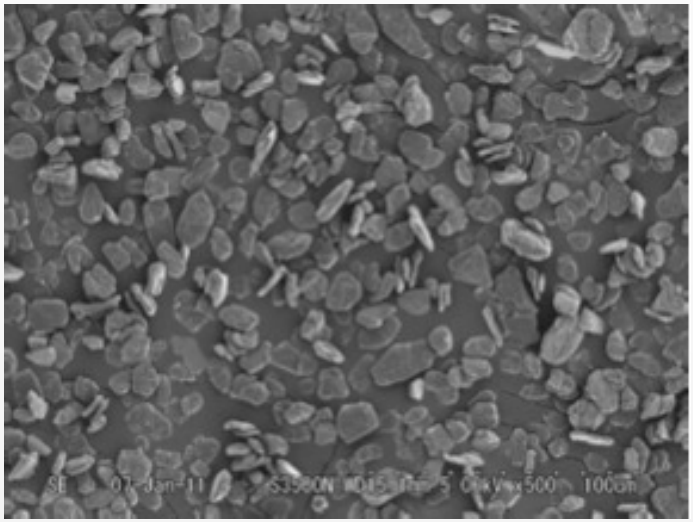
Current Generation

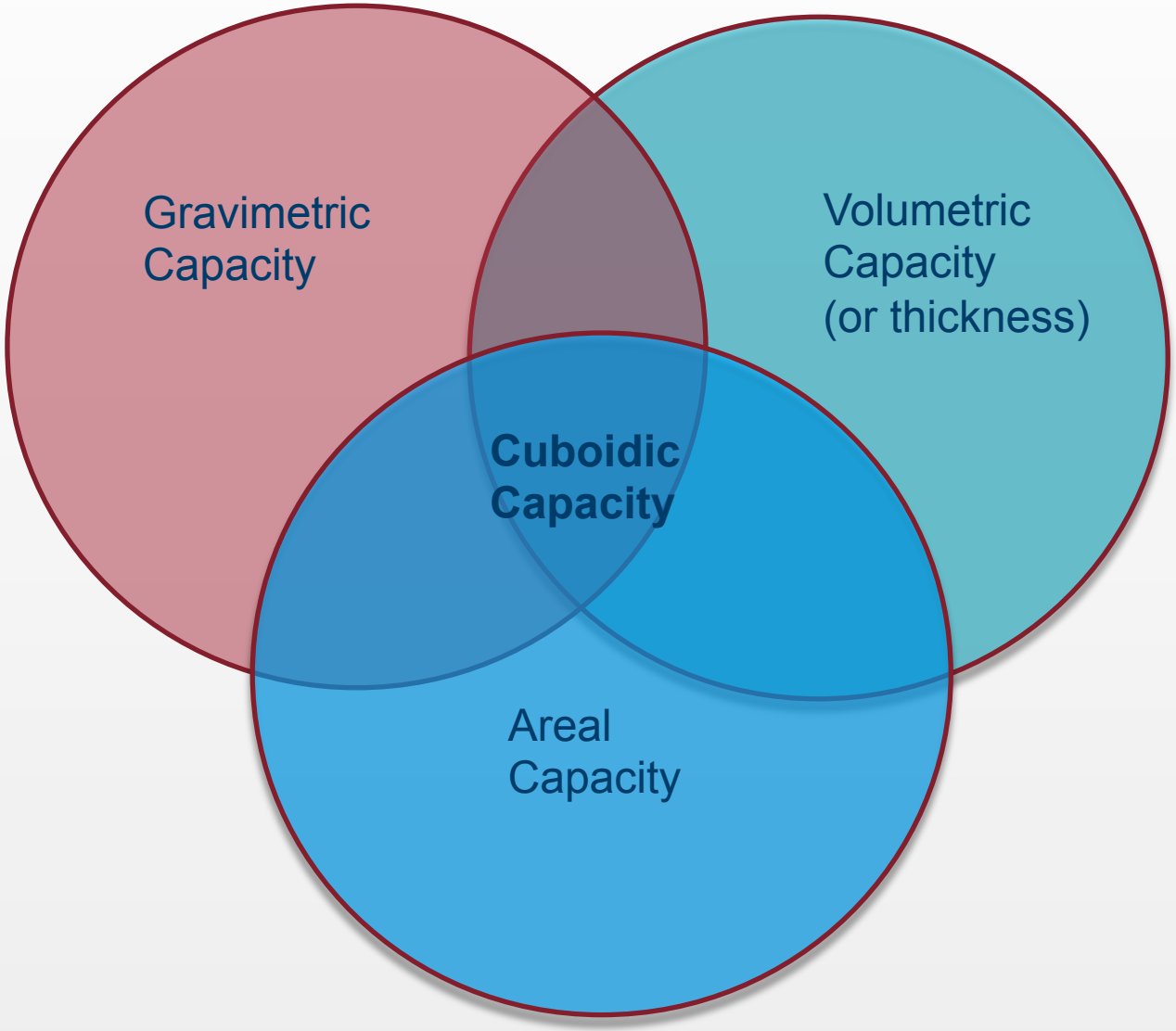
Battery grade graphite

In powder form



Printed onto copper foil

Capacity measurements



Gravimetric Capacity

- Gravimetric capacity is the amount of charge held per gram of active material.

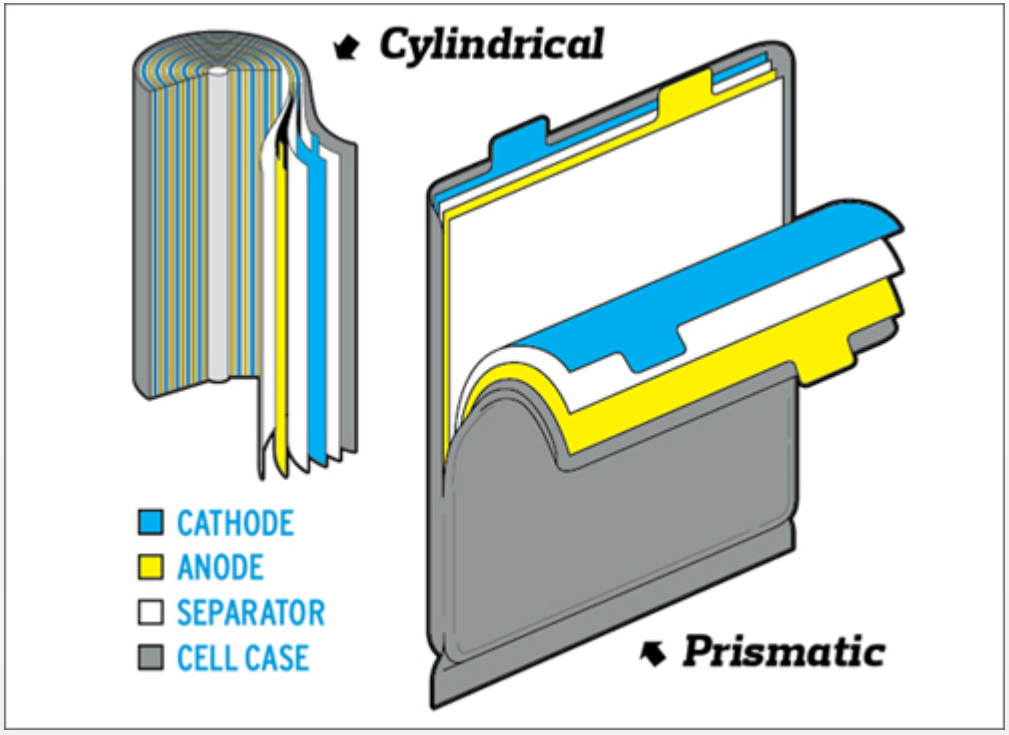
Metal	Li	Si	Al	Ge	Sn	Al	Graphite
M_xLi_y	Li	$Li_{22}Si_5$	Al_4Li_9	$Li_{22}Ge_5$	$Li_{22}Sn_5$	AlLi	LiC_6
Max. capacity (mAh/g)	>3800	>3000	2234	1600	994	993	372
Volume change	Dendritic	323	-	370	300	97	9

Increasing capacity

Current technology

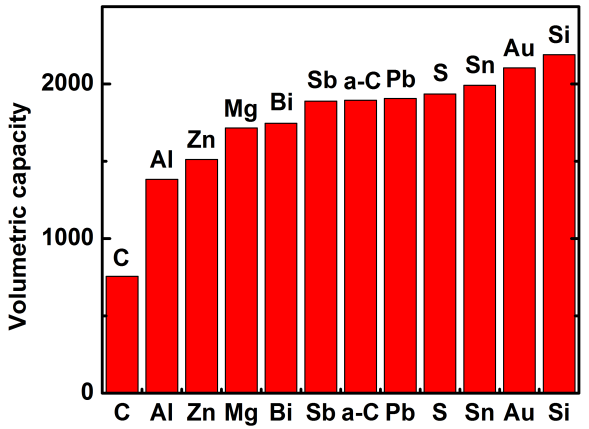
Kamali et al. Rev. Adv. Mater. Sci. 27(2011) 14-24

Cylindrical and Prismatic batteries are limited by Volume and current collector surface area



Volumetric Capacity

- Volumetric capacity is the amount of charge the cathode or anode can hold per space utilized by the active material. It is NOT the amount of charge held per volume of active material. This does not take into account the porosity of the material, which results in incorrect analysis. mAh/cm^3

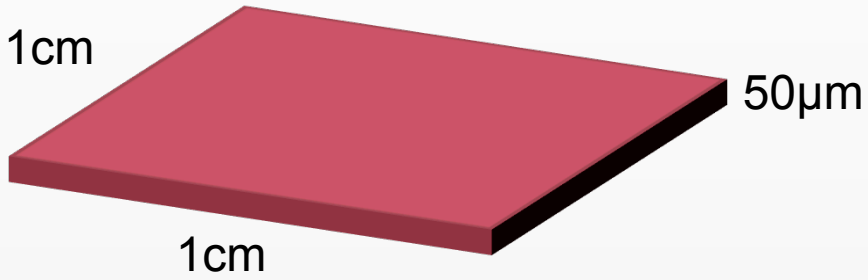


Obrovac et al. Chem. Rev. 2014, 114, 11444−11502

Areal Capacity

- Areal Capacity is the amount of charge held per active material cross-sectional area. In other words, it is the amount of active material deposited per square centimeter of current collector. The next battery electrode material must have greater than 2 mAh/cm^2 areal capacity.

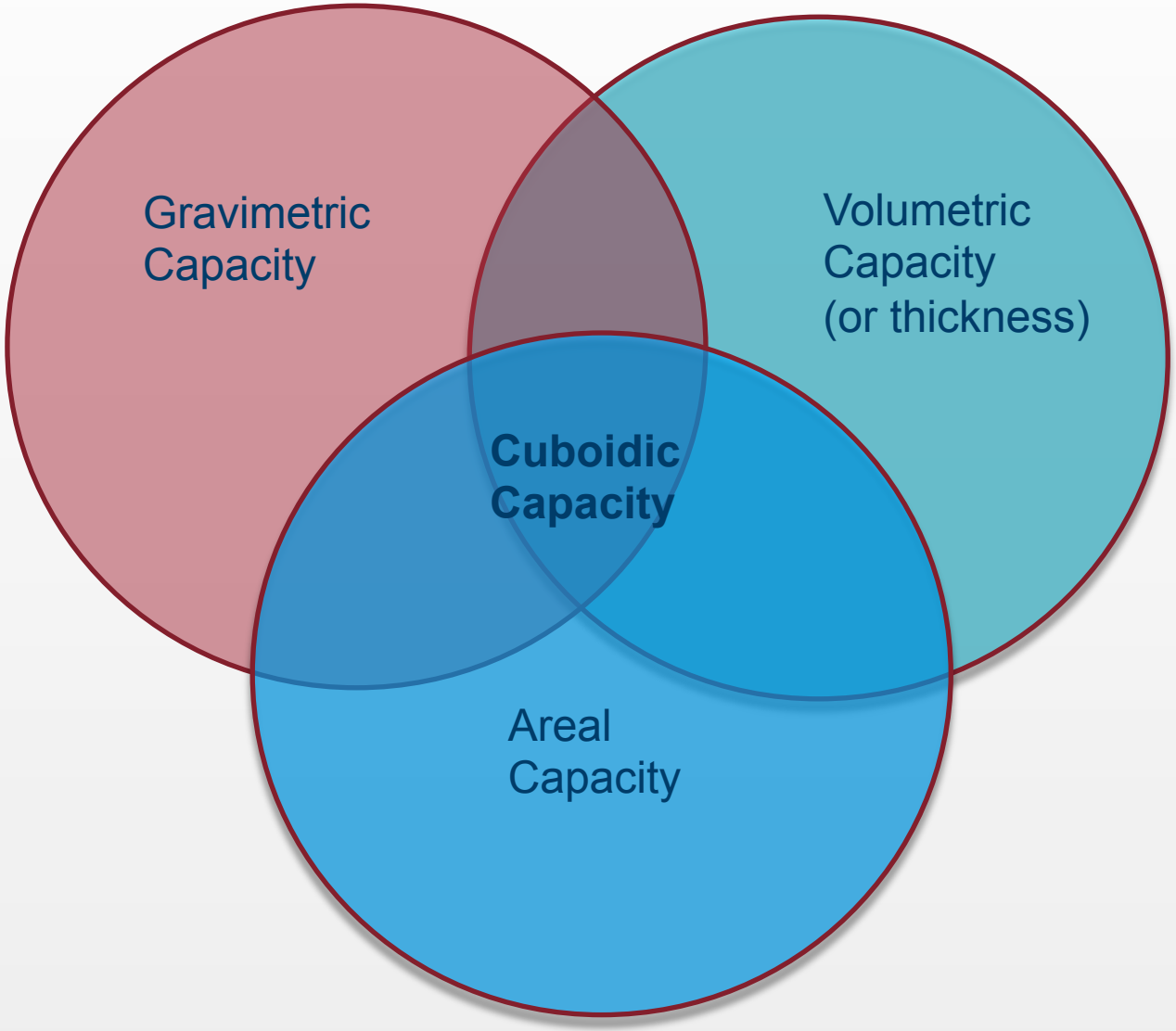
Cuboidic Capacity



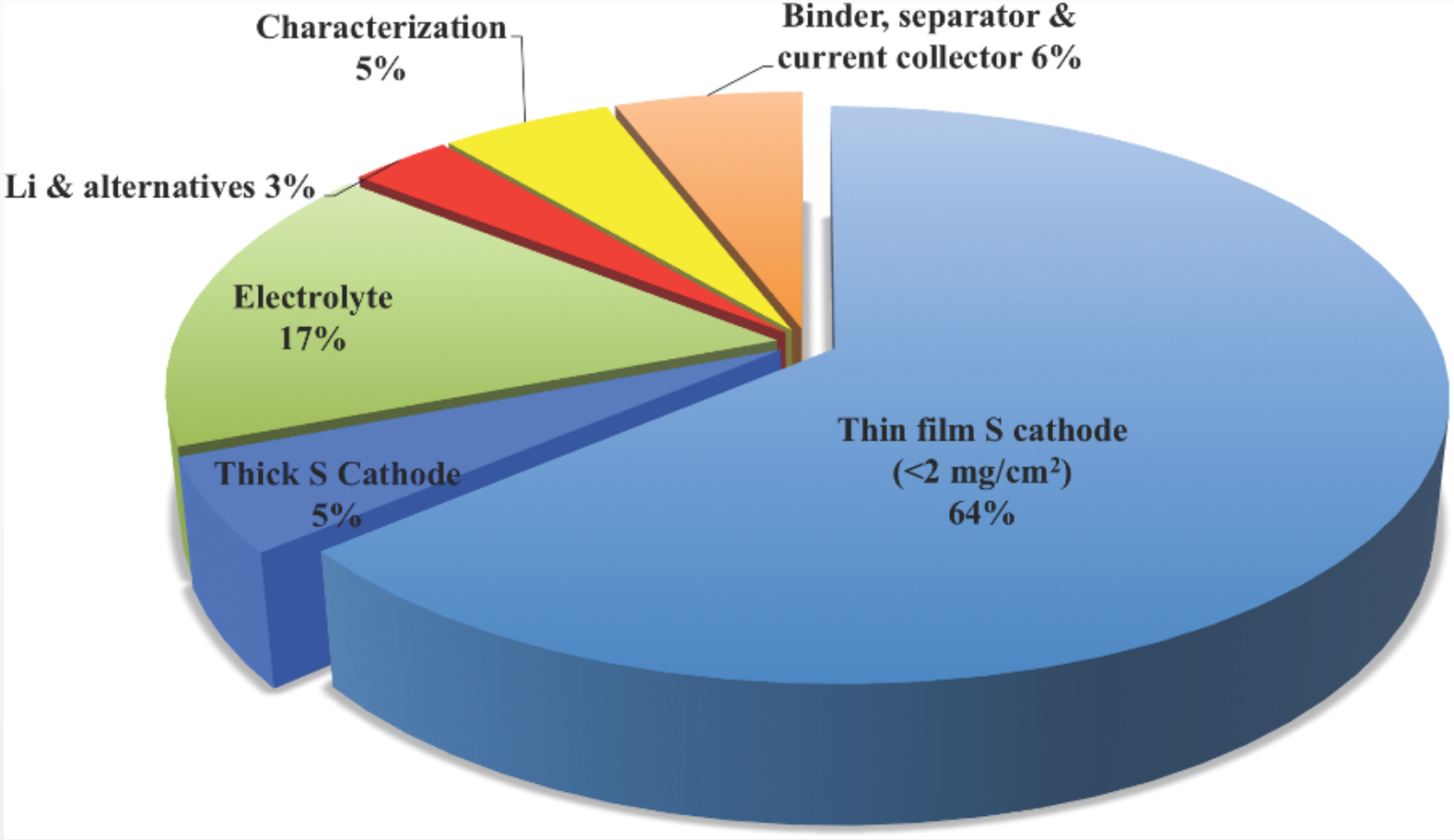
Is the amount of charge held by the active material for a limited cross-sectional area (1 cm x 1 cm) for a specific height (50 μm, which is on the order of Conventional high energy anode thicknesses)[1].

1. Singh et al. Journal of The Electrochemical Society, 162 (7) A1196-A1201 (2015)

Applying this Method to Testing New Generation Electrodes



Most battery reports do not report materials with thick enough materials.



Jie Xiou, Advanced Energy Materials Volume 5, Issue 16 2015

Films with different thicknesses have very different properties

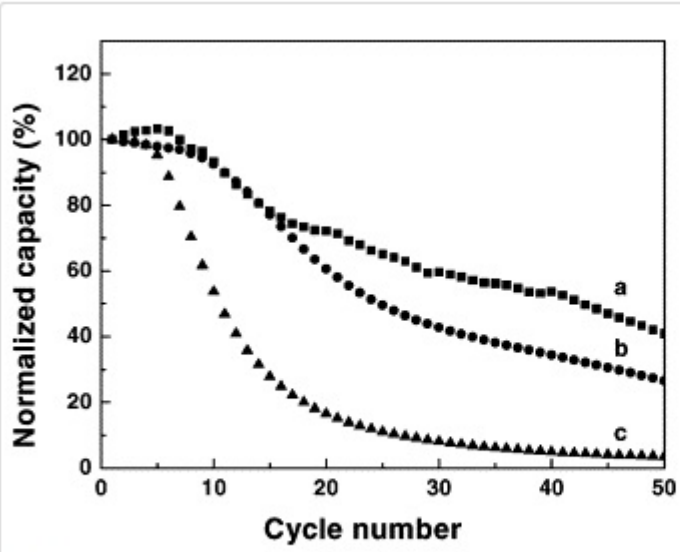
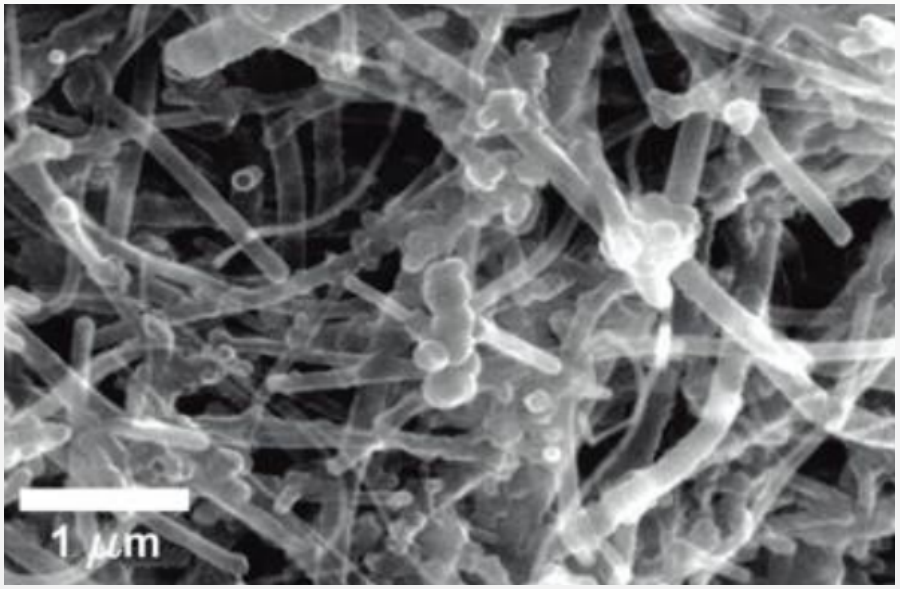


Fig. 2.

Normalised capacity vs. cycle number of tin thin-film electrodes of various thickness: (a) 300 Å; (b)700 Å; (c) 1200 Å.

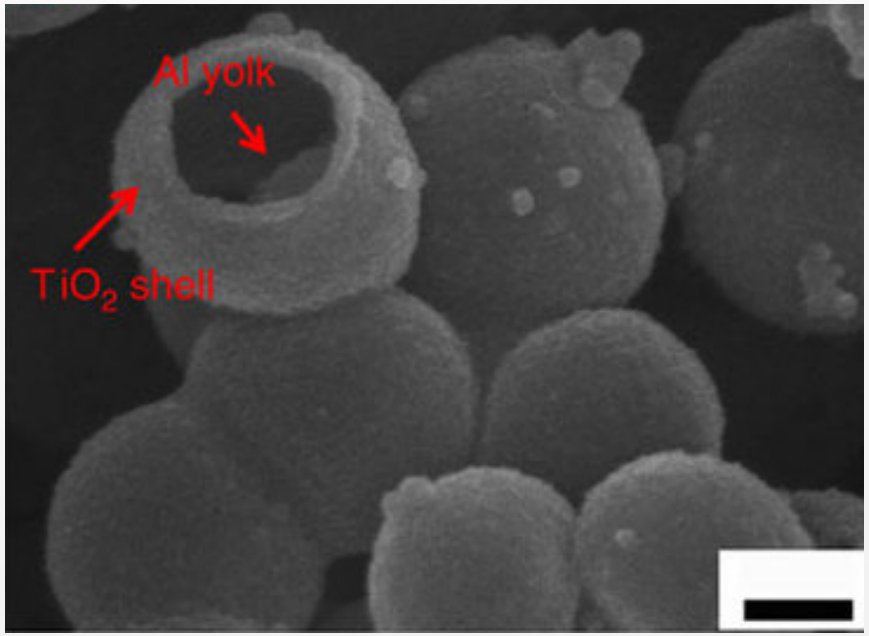
Seung-Joo Lee[a] et al. Journal of Power Sources Volume 111, Issue 2, 2002, Pages 345-349

Most nanostructured anodes do not use the available volume in an anode (ex. Carbon silicon core shell nanowires).



Cui et al. NANO LETTERS 2009 Vol. 9, No. 9 3370–3374

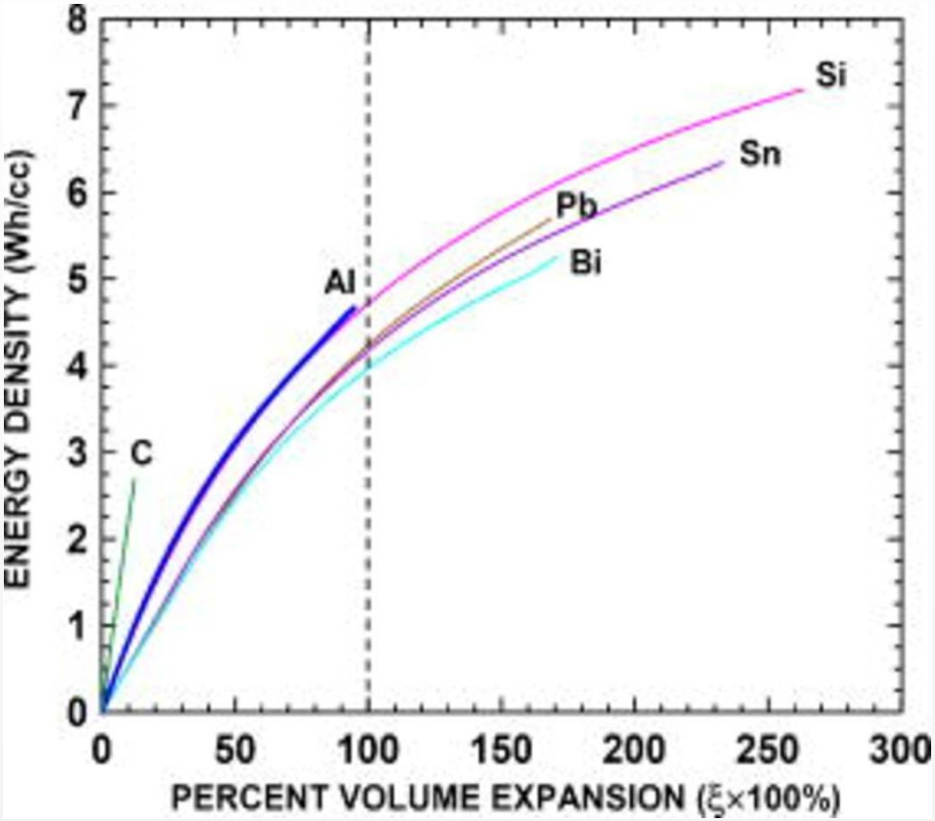
Aluminum core in a TiO_2 shell achieved 10C charge/ discharge rate with reversible capacity exceeding 650 $mAh\,g^{-1}$ after 500 cycles, with a 3 $mg\,cm^{-2}$ loading.



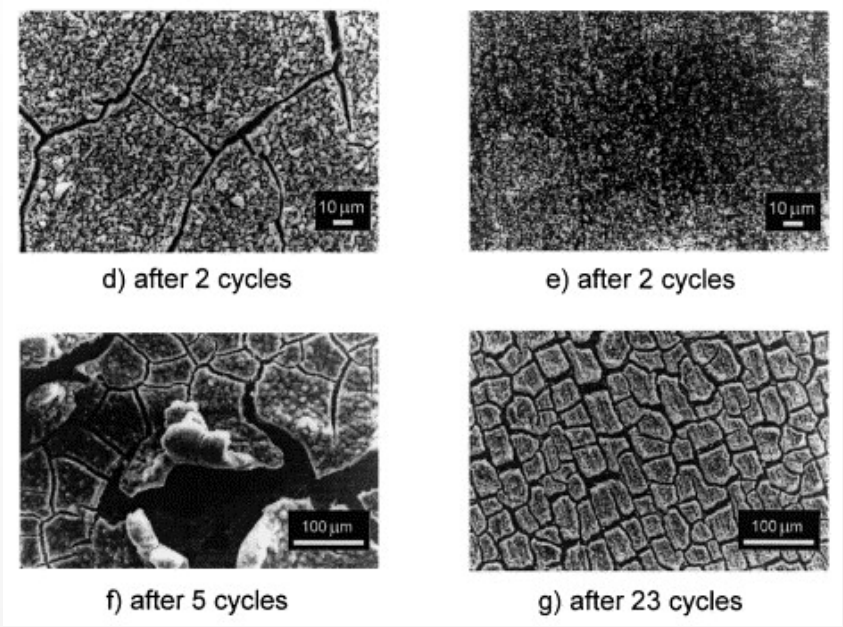
Sa Li et al. *Nature Communications* **6**, 7872 (2015) doi:10.1038/ncomms8872

Electrode	mAh/cm^2	Thickness
V6Neat	2.3	12.5
NanoNeat	1.2	4.1
V6MP	4.0	55.3
V6MM	4.1	56.7
V6MKP	3.7	51.1
V6MKM	3.8	52.5
V6HK1	4.7	65.0
V6HKCnt	4.2	58.0
NanoHK1	4.9	79.6
V6HK2	3.9	32.6
NanoHK2	2.8	29.2

Vincent L. Chevrier, et al. Evaluating Si-Based Materials for Li-Ion Batteries in Commercially Relevant Negative Electrodes. Journal of The Electrochemical Society, 161 (5) A783-A791 (2014)



Obrovac et al. Journal of The Electrochemical Society, 154 (9) A849–A855 (2007).



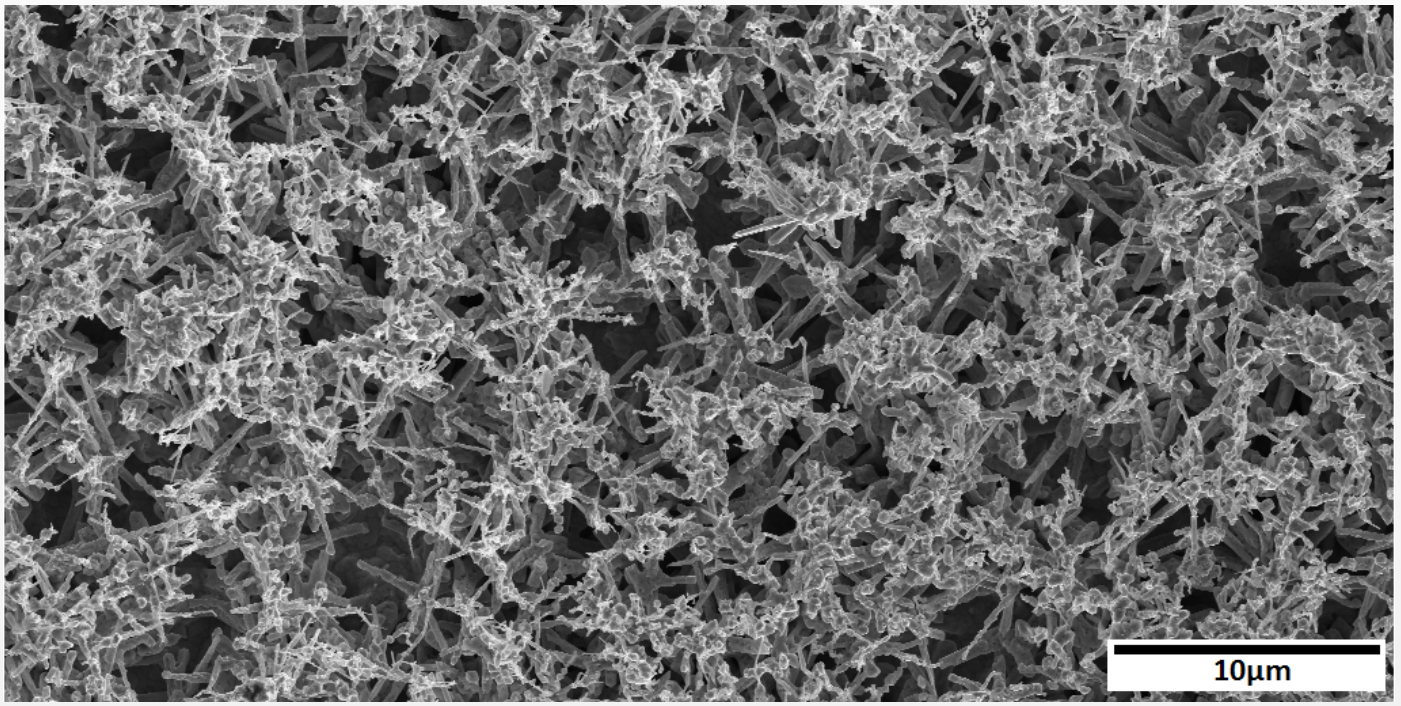
SEM images of electroplated Sn films on Cu substrate

Martin Winter , Jürgen O. Besenhard. Electrochemical lithiation of tin and tin-based intermetallics and composites. Electrochimica Acta, Volume 45, Issues 1–2, 1999, 31 – 50 http://dx.doi.org/10.1016/S0013-4686(99)00191-7

Phase	Bulk Modulus/ Shear Modulus Voigt	Increase in volume
Sn	2.566	
Li_2Sn_5	2.110	22%
LiSn	1.793	52%
Li_7Sn_3	0.95	126%
Li_5Sn_2	1.238	138%
$Li_{13}Sn_5$	1.121	142%
Li_7Sn_2	1.481	197%
$Li_{22}Sn$		258%

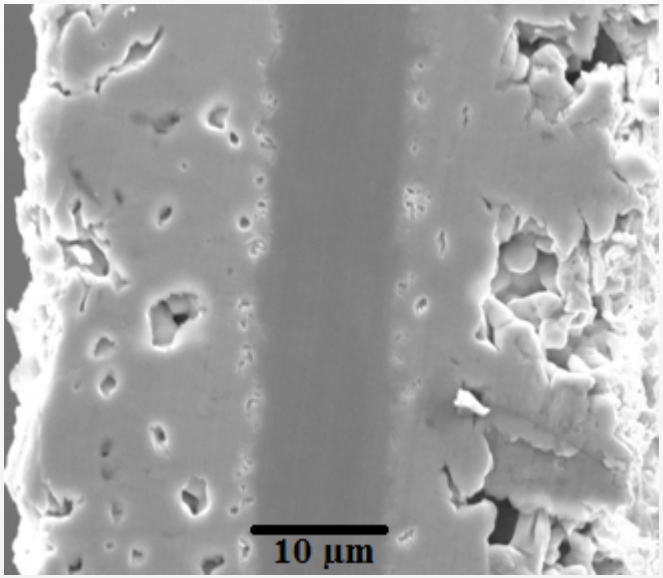
Pugh criterion B/G> 1.75 ductile, <1.75 brittle
M.E. Stournara et al. / Journal of Power Sources 208 (2012) 165–169

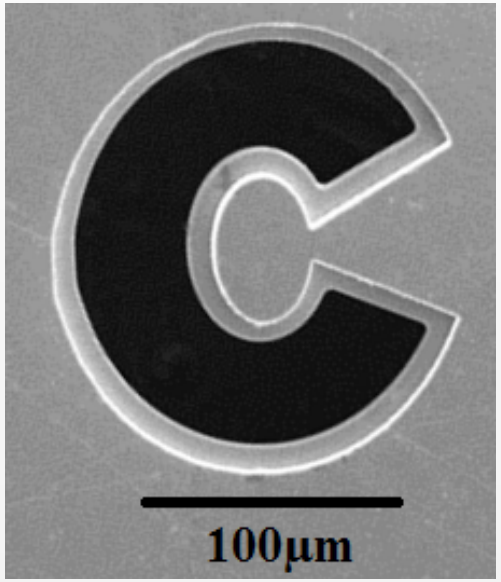
Tin Anode research

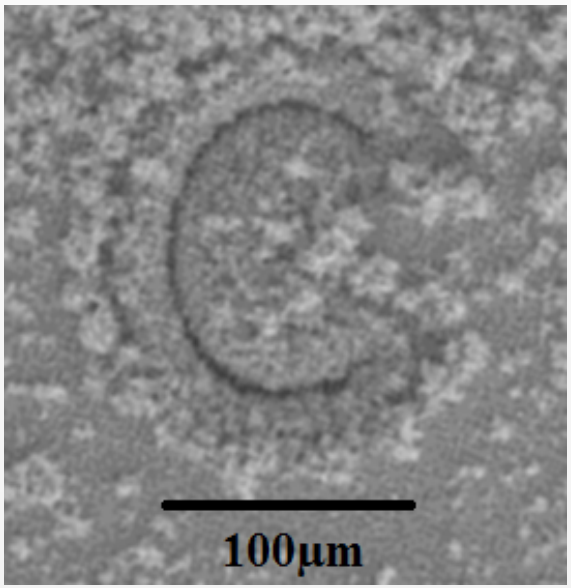


Mackay et al. J Mater Sci (2014) 49:1476–1483

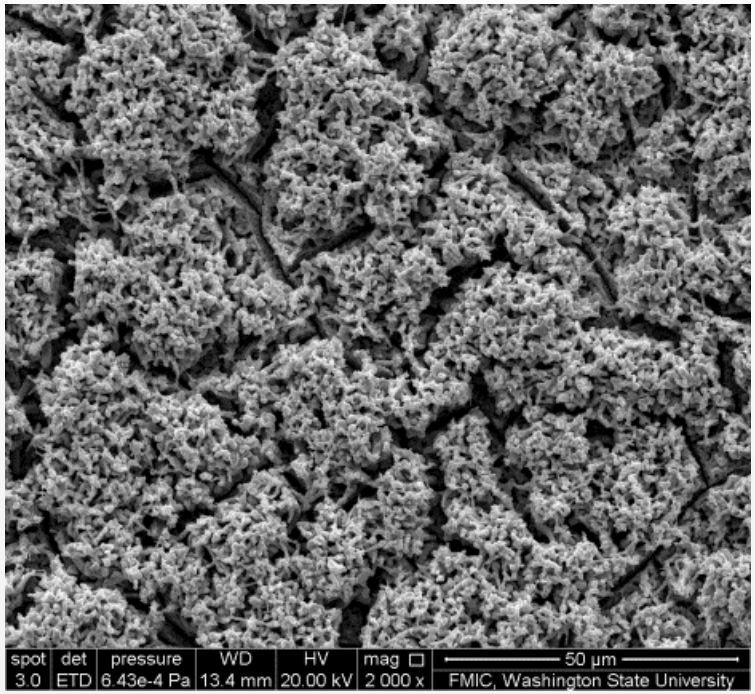
- The tin was grown onto copper foils. The needles were grown onto a 10 μm bulk tin layer and had very little porosity

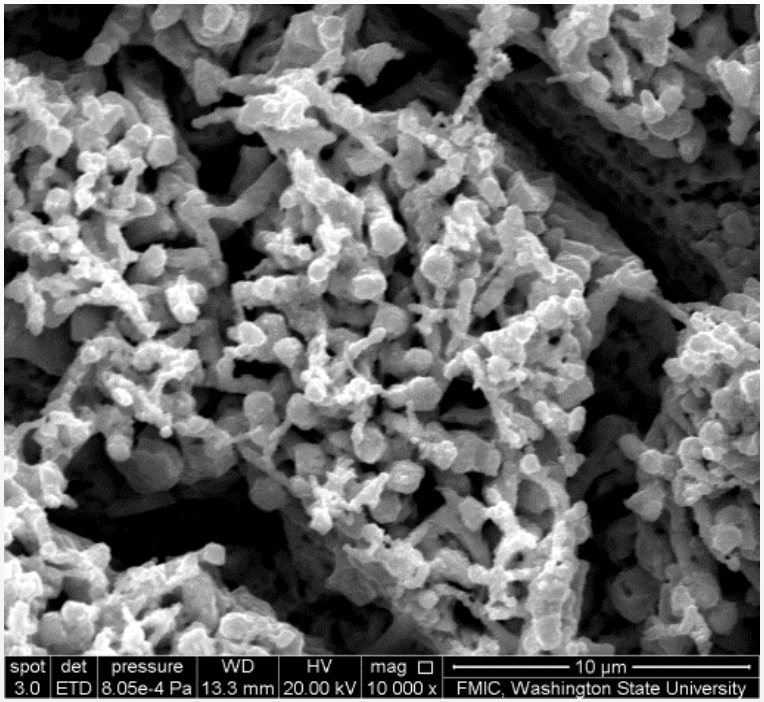




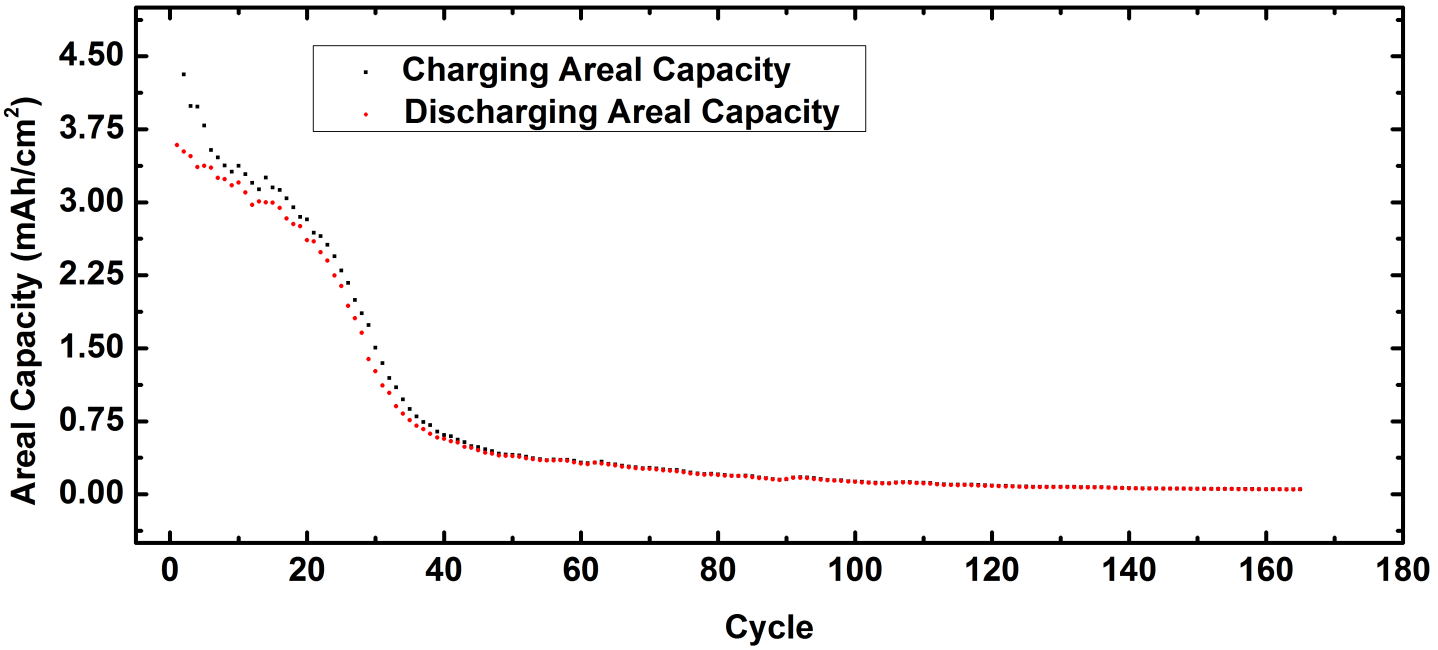


- Cracks appeared as the files were cycled.





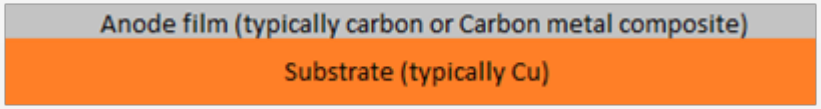
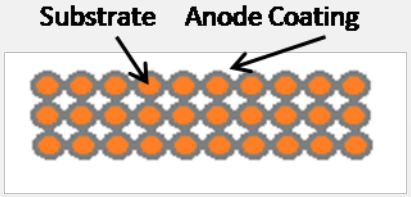
Areal Capacity



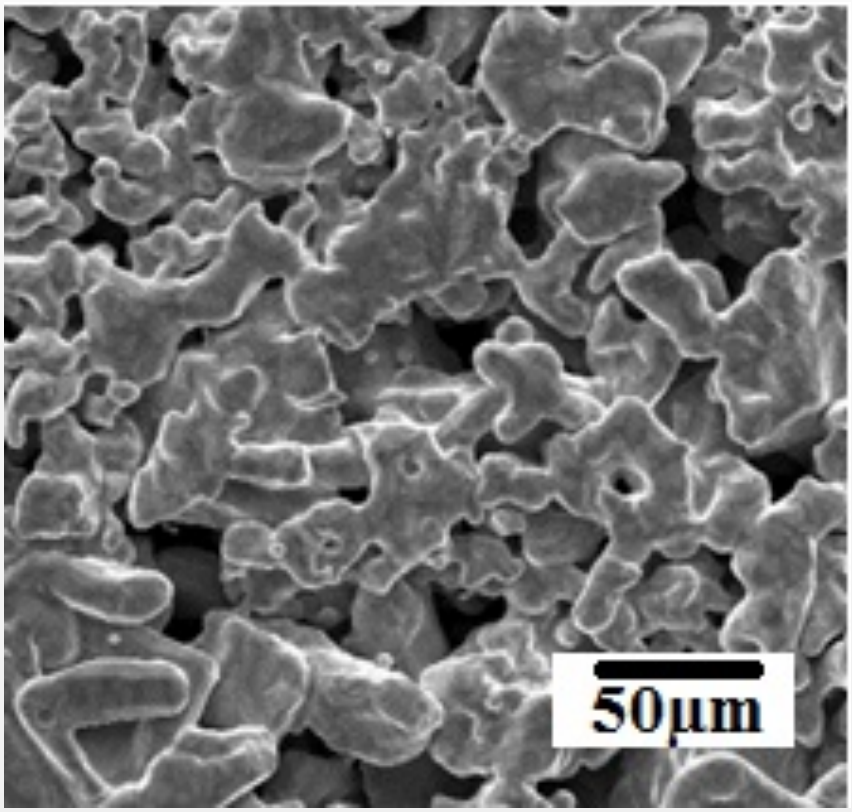
Phase	Voltage	B/G Reuss
Sn	0.69	2.561
Li_2Sn_5	0.53	2.110
LiSn	0.43	1.888

Performance of tin-containing thin-film anodes for rechargeable thin-film batteries
Seung-Joo Lee[a] et al.

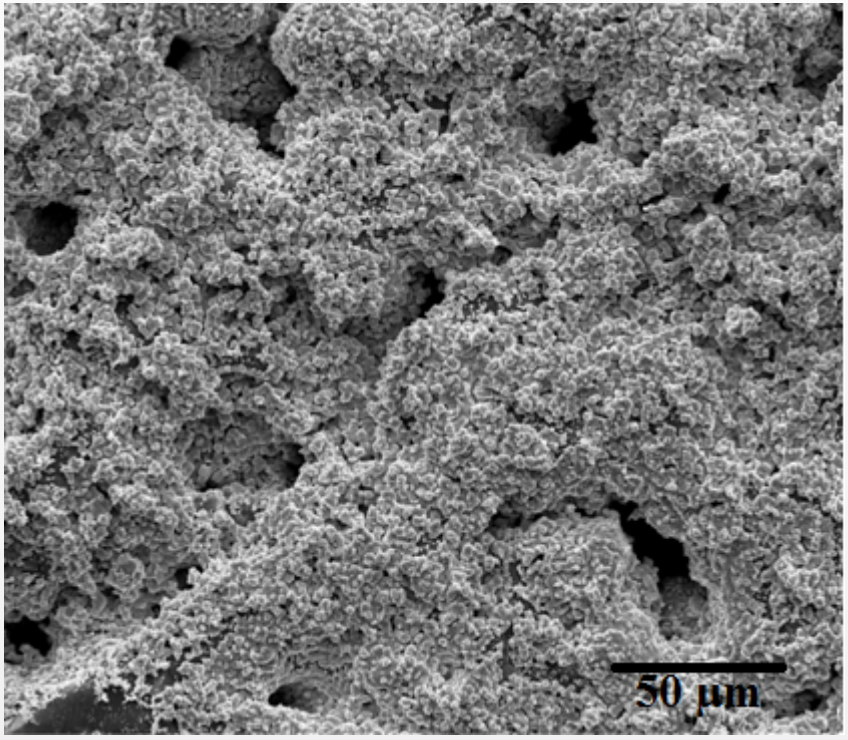
We made a porous substrate and then electroplate on top to increase the areal capacity and volumetric capacity.

Anode Profile Structure	Gravimetric capacity	Volumetric capacity	Areal capacity
Flat current collector with nanostructured active material (typically metallic based) 	High	Low	Low
Flat current collector with active material film (typically carbon or carbon composite based) 	Low	High	High
Porous current collector with active material film (metallic) 	Low	High	High

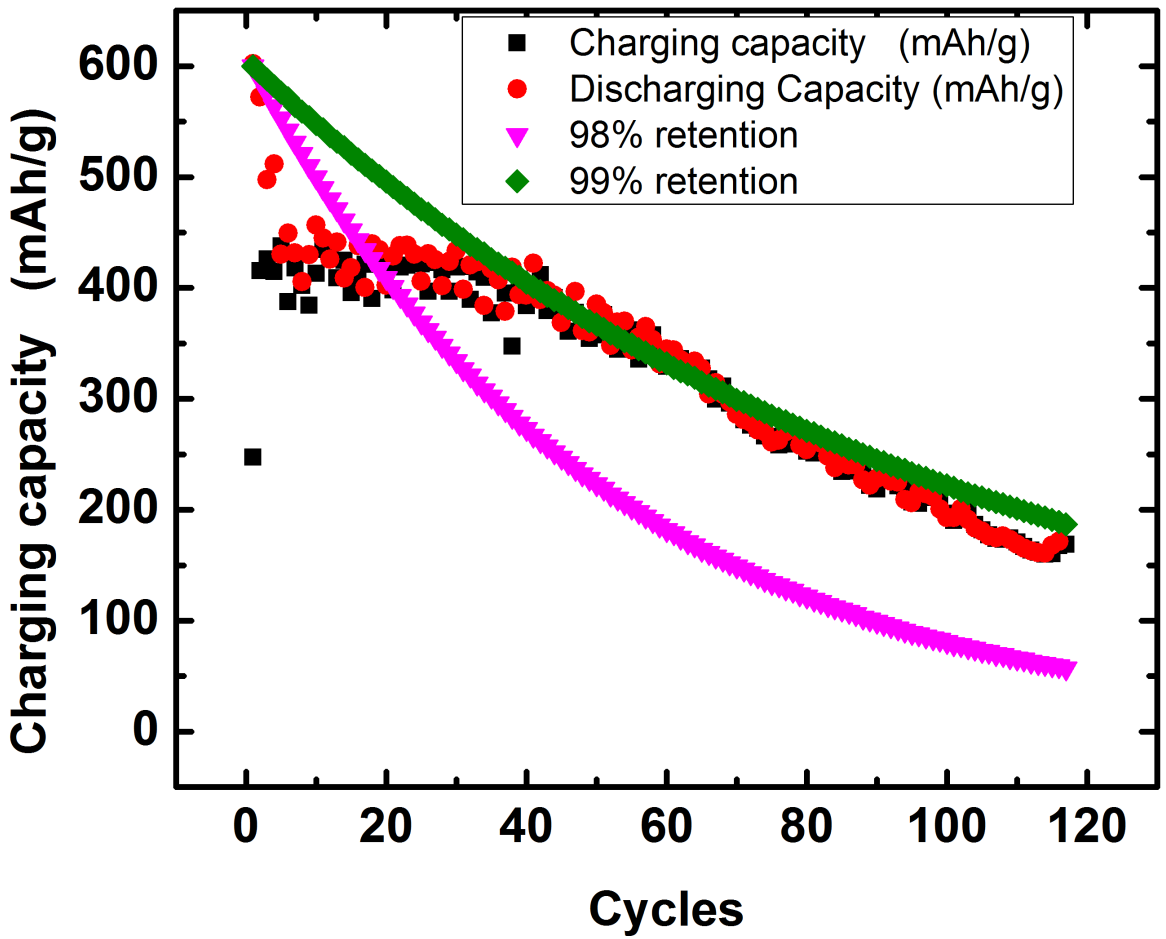
Titanium substrate before electrodeposition

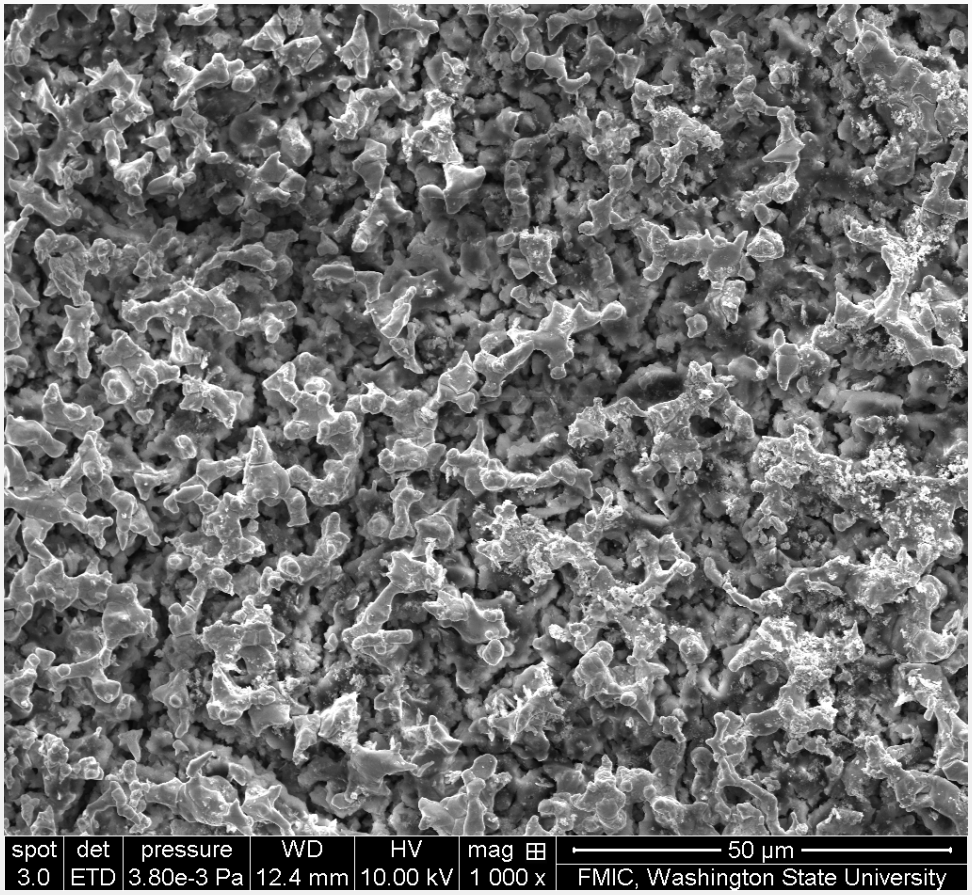


Titanium battery before cycling with a 20 mg of tin electroplated onto titanium substrate.

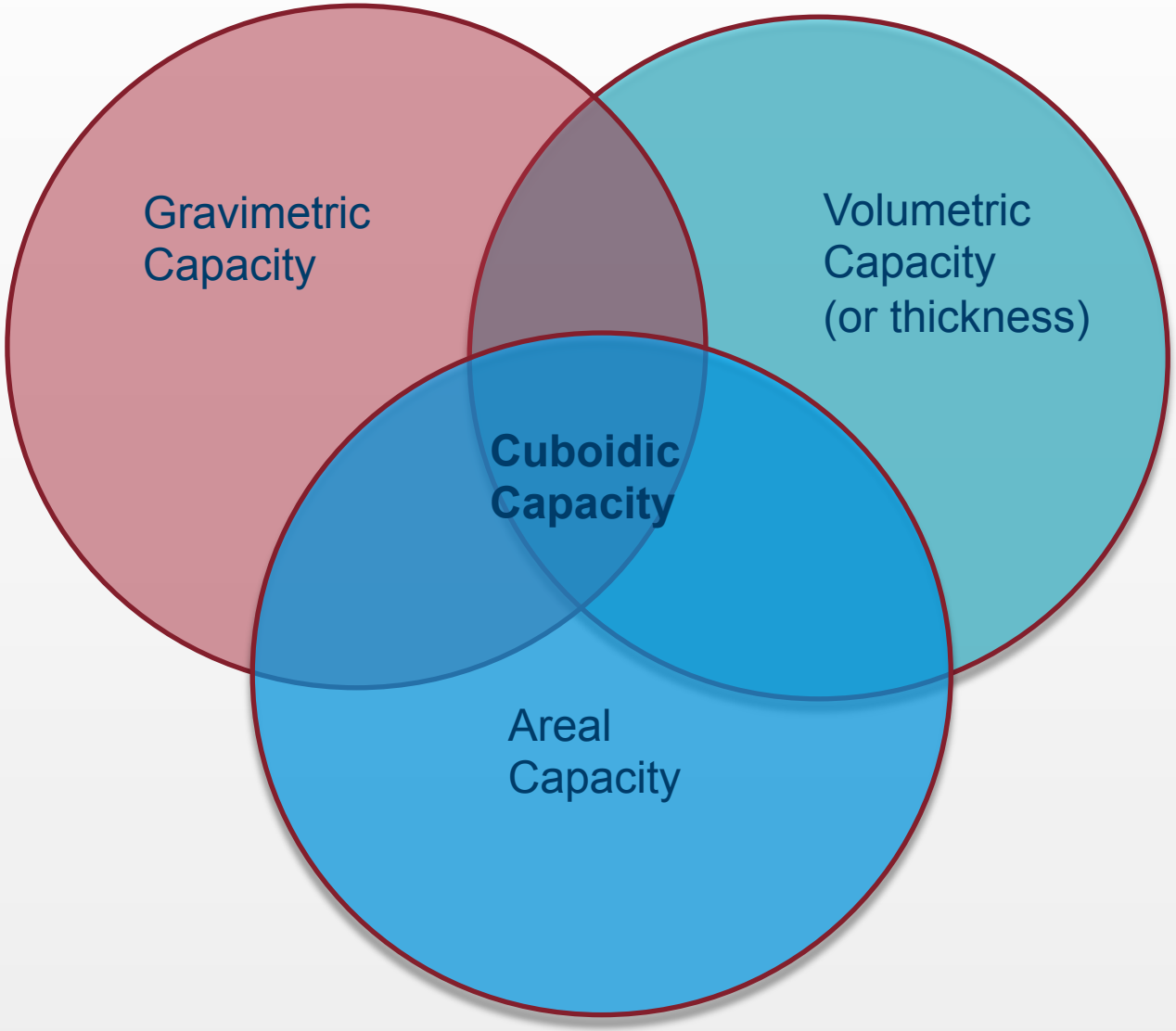


Capacity


Charging capacity (mAh/g)
Discharging Capacity (mAh/g)
98% retention
99% retention
Charging capacity (mAh/g)
600
500
400
300
200
100
0
0
20
40
60
80
100
120
Cycles


spot
3.0
det
ETD
pressure
3.80e-3 Pa
WD
12.4 mm
HV
10.00 kV
mag
1 000 x
50 µm
FMIC, Washington State University

Applying this Method to Testing New Generation Electrodes



Questions