Fabrication of Porous Hollow Glass Microspheres as additives for Lead Acid Battery

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Outline

- Why Lead Acid Battery (LAB)
- What limits the performance of Lead Acid Battery
- Why Porous Hollow Glass Microspheres (PHGMS)
- How to fabricate PHGMS
- Preliminary Results
- Potential applications of PHGMS
- Future work
- Acknowledgment

Why lead acid battery?

Plug in Hybrid Electric Vehicles (PHEV)
reduce energy consumption in transportation.

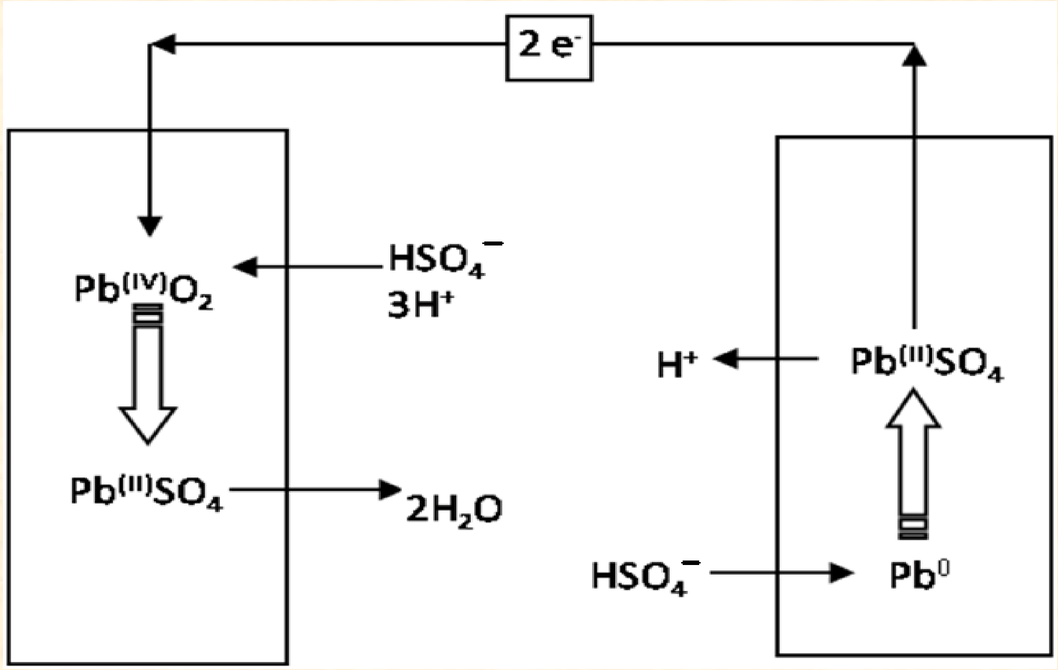
	LAB	NiMH	Li-Ion
Specific power	70-100 W/kg	120-150 W/kg	150-250 W/kg
Cost	181 $/kWh	>725 $/kWh	>725 $/kWh
Specific energy	25-35 Wh/kg	65-75 Wh/kg	100-150 Wh/kg

http://www.google.com/imgres?imgurl=http://earth911.com/wp-content/uploads/2009/04/plug-in_hybrid_electric_vehicle

J. Garche, Physical Chemistry Chemical Physics, **3** (2001) 356-367.

- Advantages
  - ❖Safe
  - ❖Low cost
  - ❖High power density
  - ❖Wide operating temperature range
  - ❖Environmentally friendly (Recyclable)
  - ❖No memory effects
- Disadvantages
  - ❖Low specific energy
  - ❖Shorter life time when deep discharged

Lead Acid Battery chemical reaction



Positive Plate

Negative Plate

Half-reaction of Positive electrode:

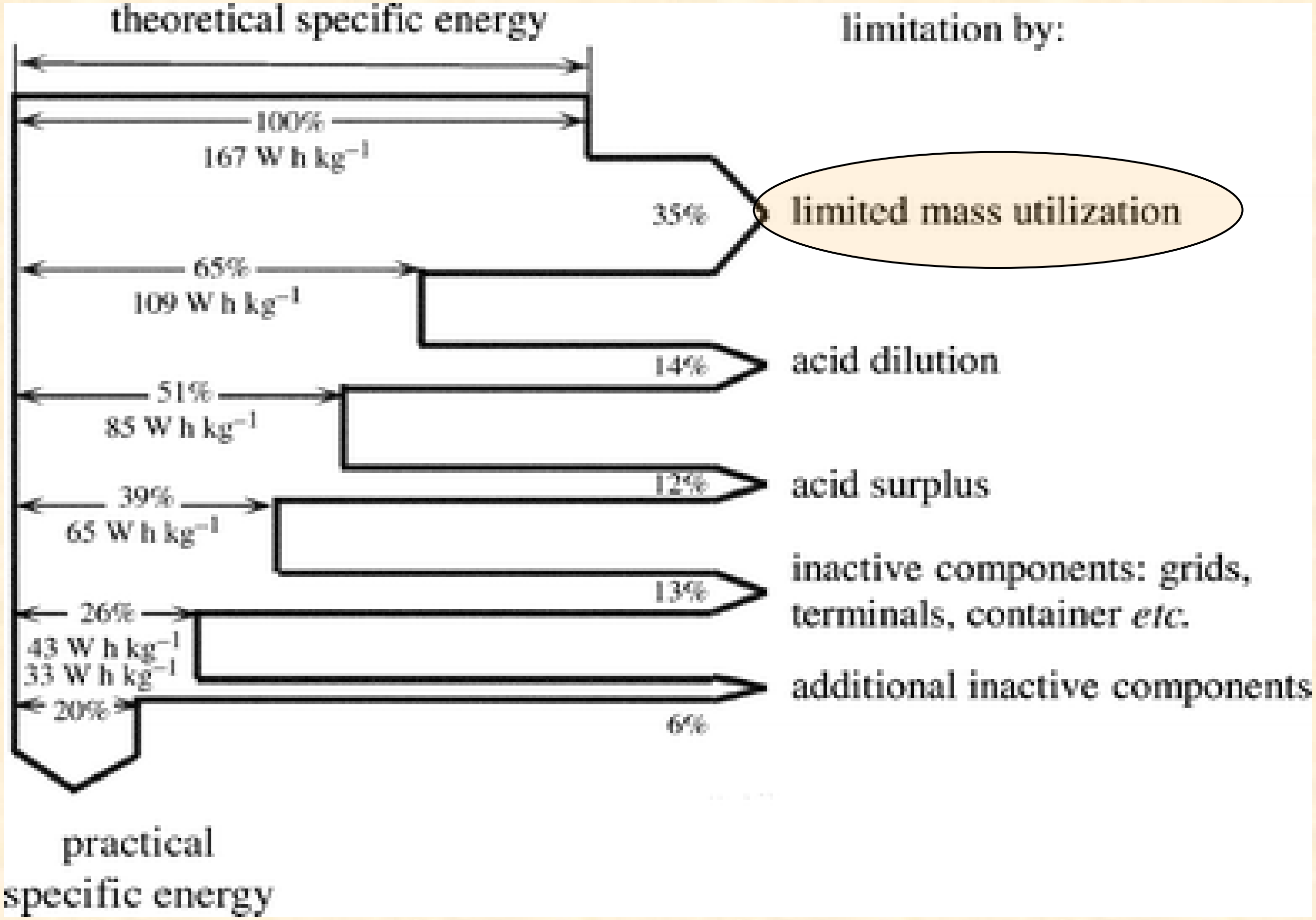
$PbO_{2\,(s)} + HSO_4^-{}_{(aq)} + 3H^+ + 2e^- \rightarrow PbSO_{4\,(s)} + 2H_2O_{(l)}$ **E^0 = 1.675V**

Half reaction of negative electrode:

$PbSO_{4\,(s)} + H^+ + 2e^- \rightarrow Pb_{(s)} + HSO_4^-{}_{(aq)}$ **E^0 =-0.355V**

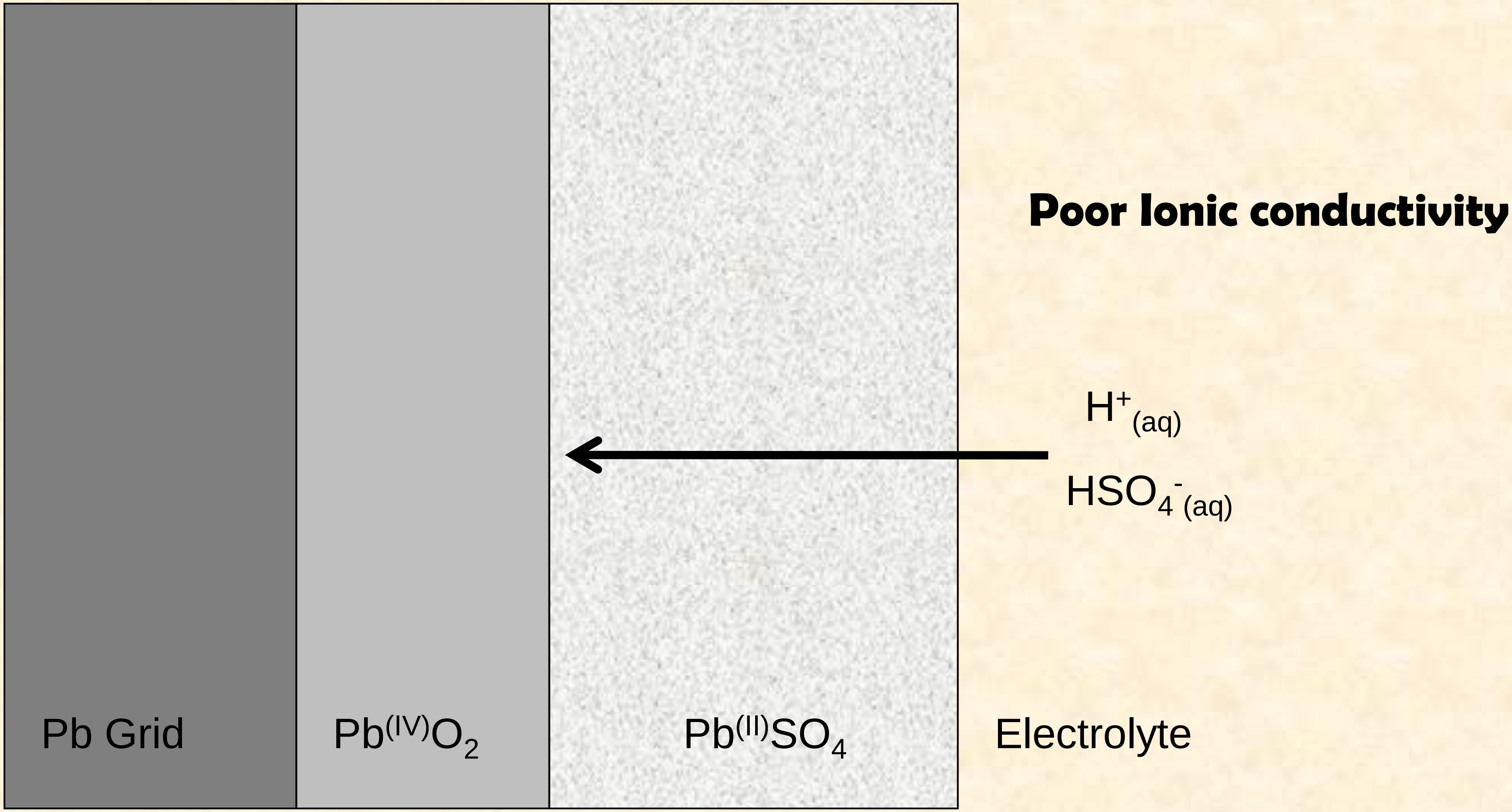
Full cell potential is around 2 V depending on the concentration of electrolyte

What limits the specific energy of the LAB?



Jürgen Garche, J. Phys. Chem. Chem. Phys., ***3****, (2001) 356-367*

Problems



S.D. McAllister, R. Ponraj, I.F. Cheng, D.B. Edwards, J. Power Sources, **173** (2007) 882-886.

Solutions – Additives

- Improve the porosity of the battery paste
- Increase the ratio of active materials/H_2SO_4
- Decrease the weight of battery

Requirements for positive plate additives

- Stable
- Cheap
- Light
- Good adhesion to battery paste

Literature review on positive plate additives

Additives	Loading Wt. %	Increasing in utilization % (high rate discharge)	Stability
Carboxymethyl cellulose	0.2	9.9	No
Carbon Black	0.1	3.3	No
Silica gel	0.2	10	Yes
Diatomaceous earth particles	3	12.7	Yes

*Wang Qing, J. of Wuhan University of Technology--Materials Science Edition, **22** (2007) 174*
*H.Dietz, J.Garche, K.Weisner, J. Power Sources, **14** (1985) 305*
*Simon D. McAllister, Rubha Ponraj, I. Francis Cheng and Dean B. Edwards, J. of Power Sources **173**, 2* (2007)

Hollow Glass Microspheres used as an additive in LAB positive paste

Figure of merit and utilization (0.1 A g^{-1})

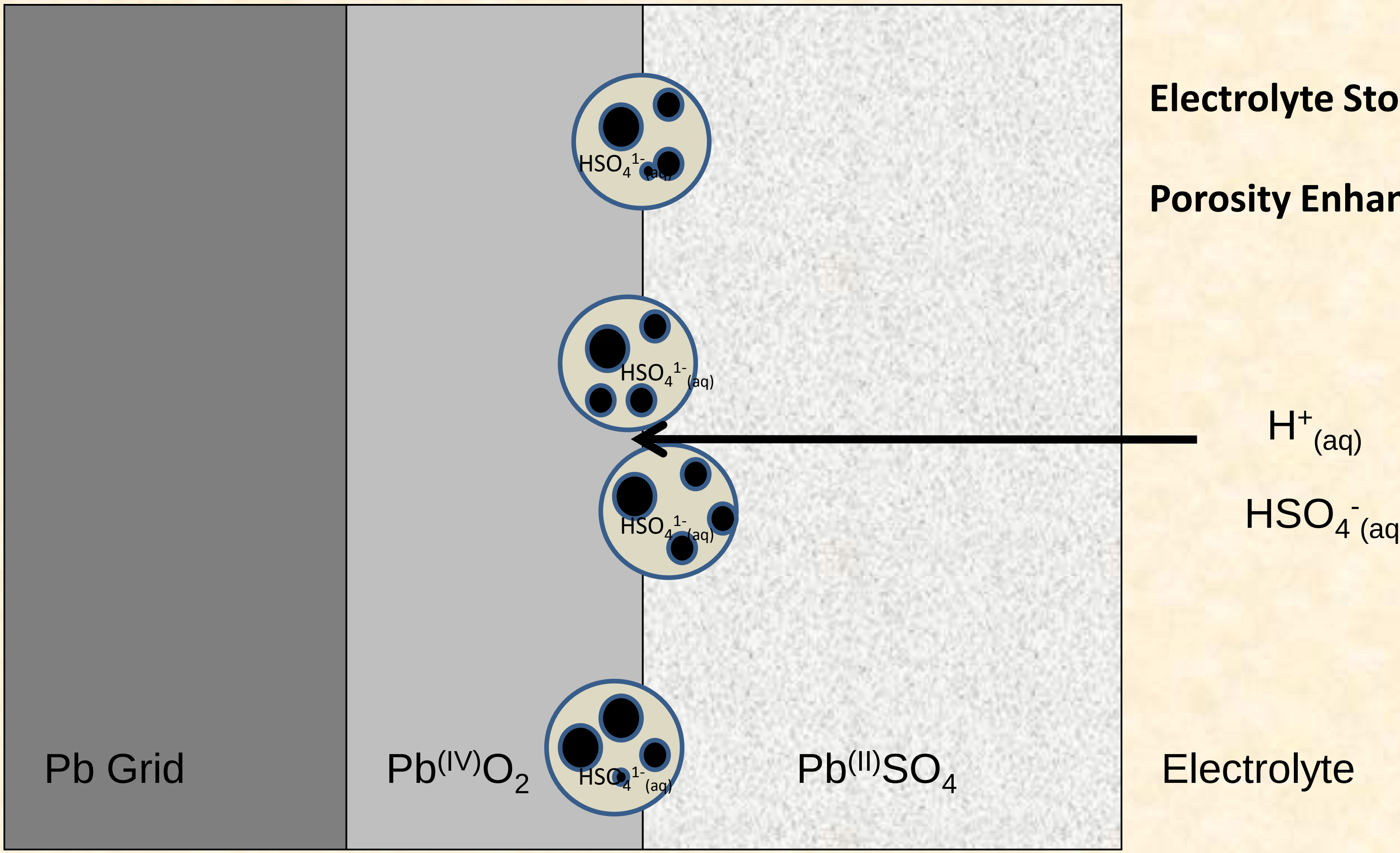
Plate type	Pore volume (cm^3)	Porosity (%)	Paste weight (g)	Figure of merit (%)	Pore utiliz. (%)	Measured utiliz.[a] (%)
Production plate	7.325	30.52	84.61	11.25	9.86	11.64
Hand pasted, 0% glass microspheres loading	5.4127	22.72	80.2	8.72	7.65	5.02
Hand pasted, 1.1% glass microspheres loading	6.087	25.84	64.1	12.34	10.81	24.57
Hand pasted, 2.2% glass microspheres loading	6.102	26.89	58.4	13.58	11.9	30.32
Hand pasted, 4.4% glass microspheres loading	5.918	26.41	35.21	16.8	14.73	33.12
Hand pasted, 6.6% glass microspheres loading	6.5476	28.85	35.13	24.22	24.22	19.94

*D.B. Edwards, V.S.Srikanth, J. Power Sources, **34** (1991) 217*

Porous Hollow Glass Microspheres

Electrolyte Storage

Porosity Enhancer



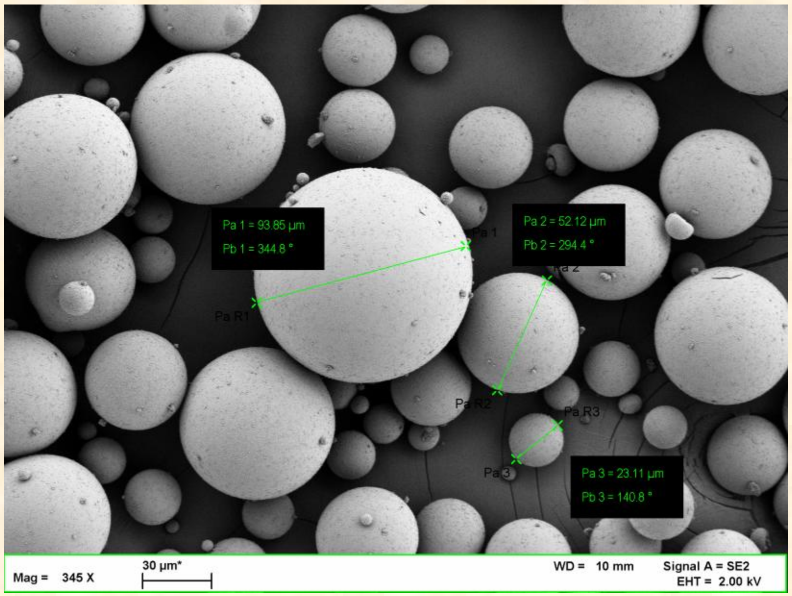
Model predicts that 23% v/v loading of PHGMS increasing specific energy by 40%

Troy C. Dayton, Dean B. Edwards, *J. Power Sources*, ***85*** *(2000) 137- 144*

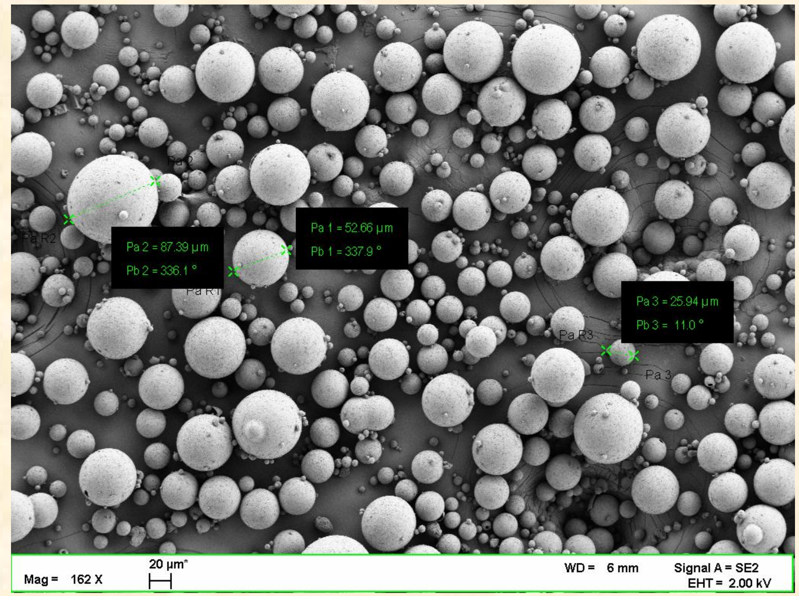
Fabrication of PHGMS

Starting materials: Hollow Glass Microspheres(HGMS) From 3M

K25



S38



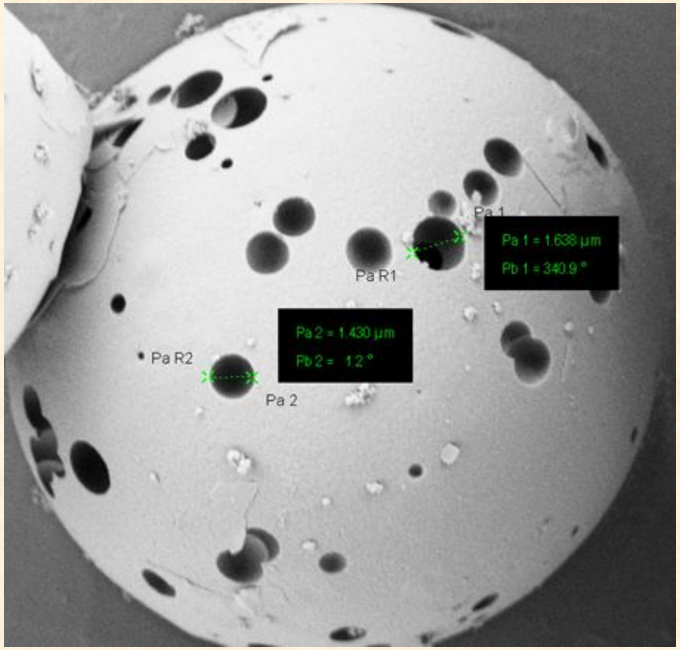
Products	Average Size (µm)	Isostatic Crush steength (psi)	Density (g/cm^3)	Wall thickness (µm)
K 25	55	750	0.25	1
S 38	40	4000	0.38	1

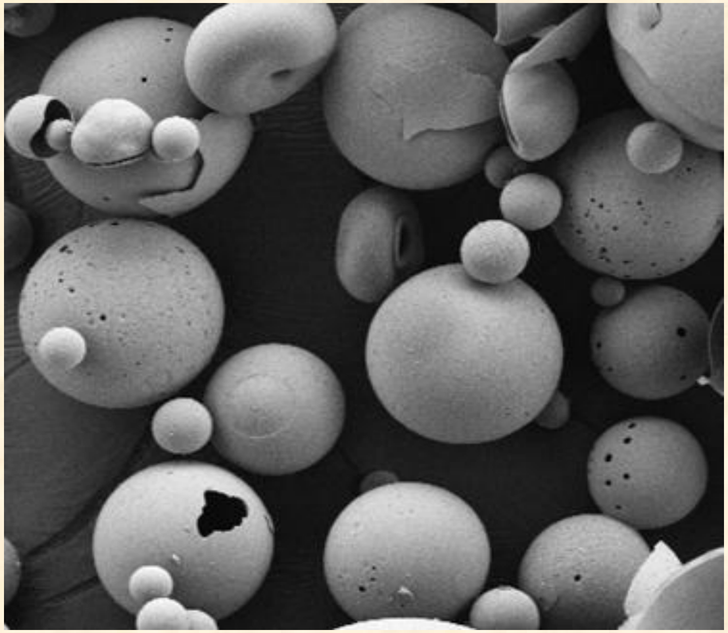
Chemical etching

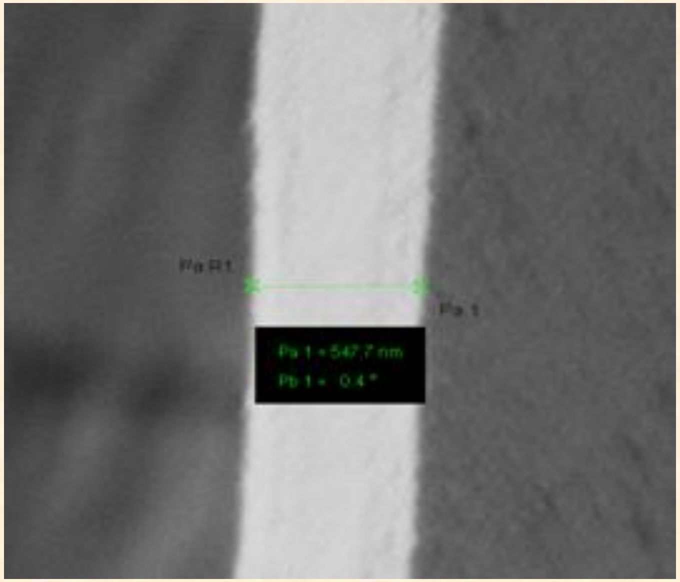
Easy process

- 1% HF
- Shaking on the bench top shaker for 20 min
- Separation of PHGMS and HGMS
  - Floaters---HGMS
  - Sinkers--- PHGMS
- Yields 40%

K25 PHGMS

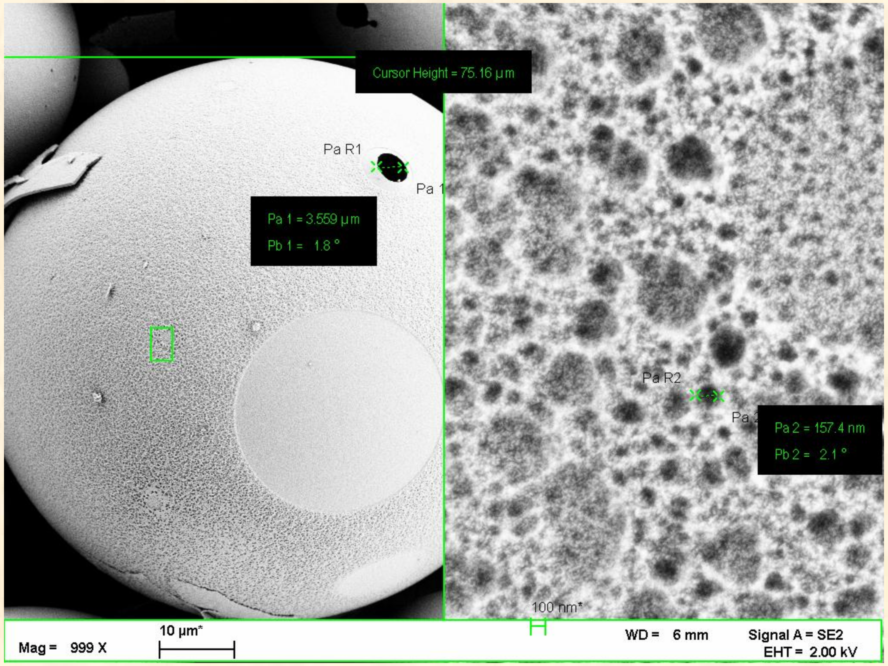


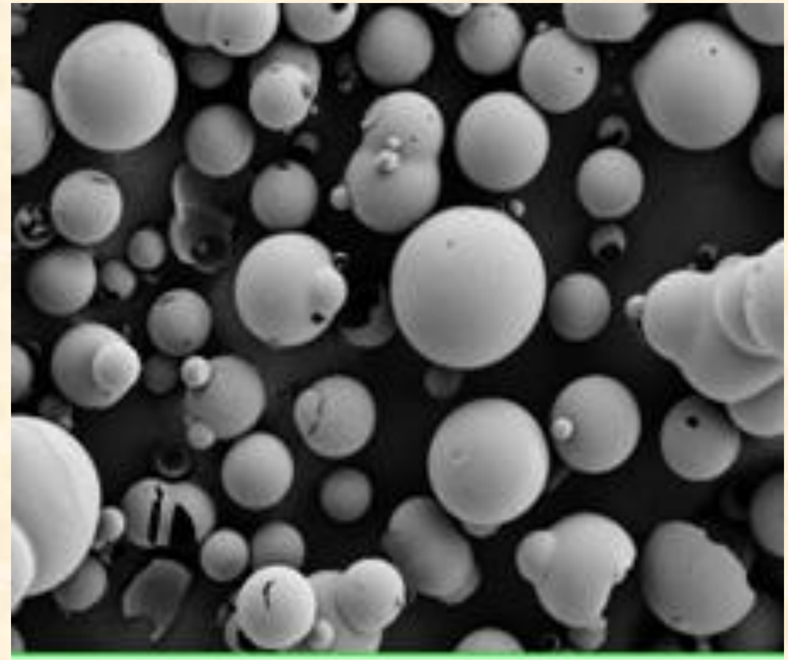


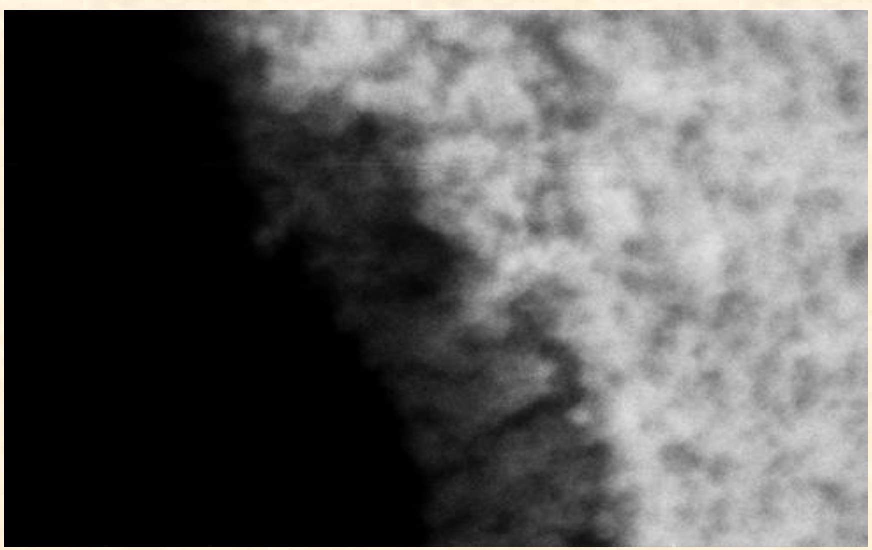


After etching
SEM pictures
- Micro-pores coverage on the surface
- Pores size 1-2 µm
- Low Breakage

S38 PHGMS

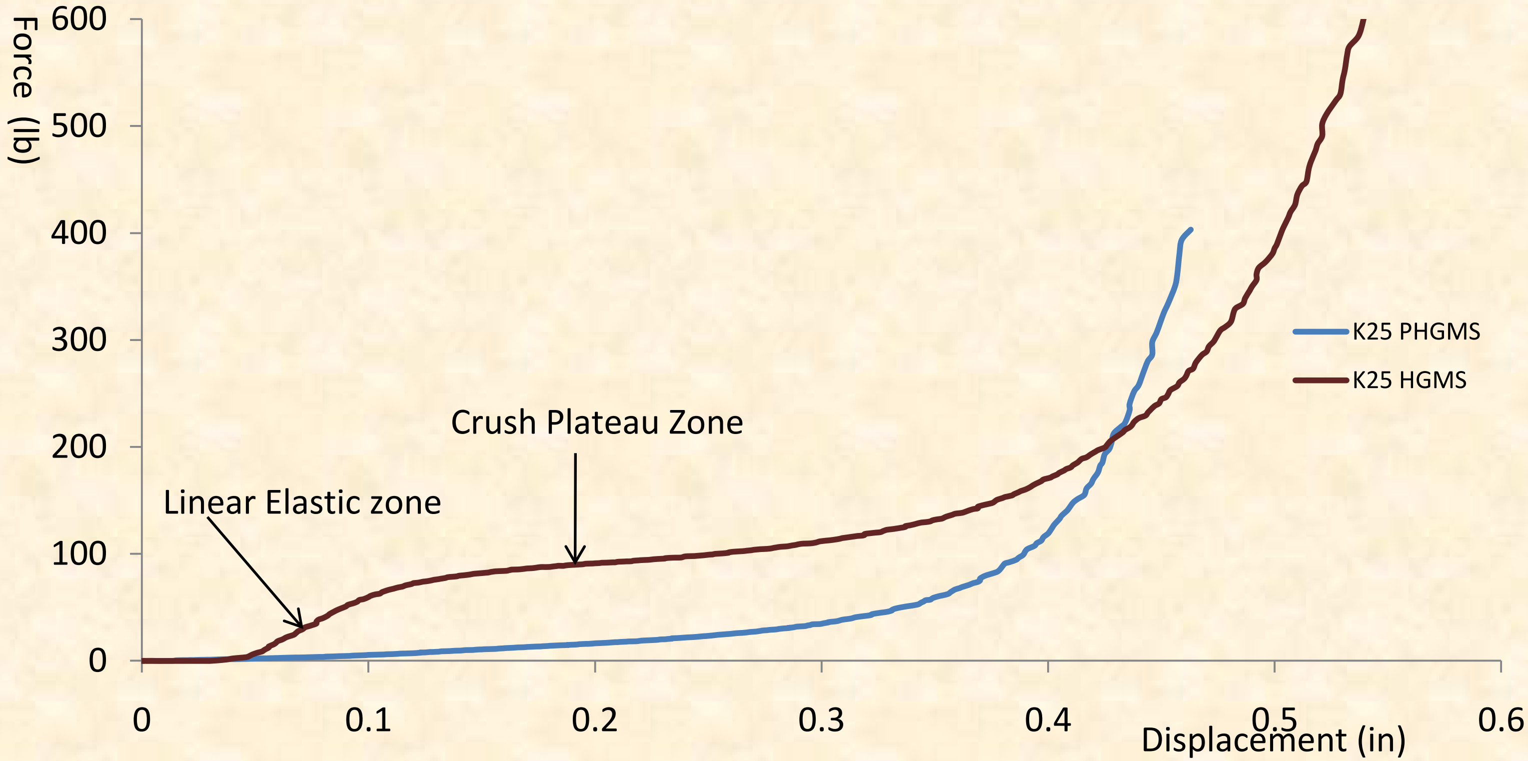






After etching SEM pictures
- Meso-pores surface
- Pores size around 200nm
- Low Breakage
- Spongy wall cross section

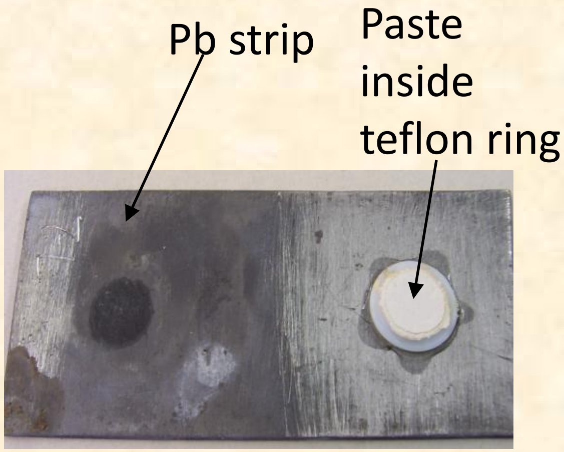
Crush strength Of k25phgms



Sample	K25 as received	K25 PHGMS
Crush Strength (lb)	100	16

V. O. Ikem, A. Menner, A. Bismarck. *Langmuir* 2010, **26**(11), 8836-8841

Performance Enhancement of K25 PHGMS as Additives in LAB Positive Plates



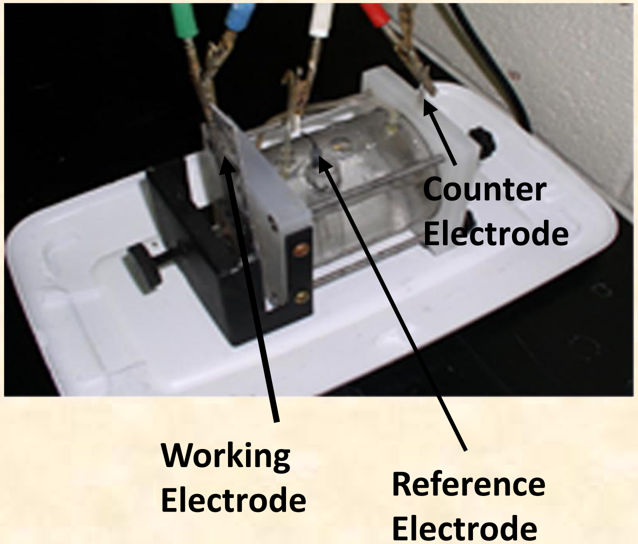


Plate	Additives	Loading V/V %	Increase in 66 mA/g Utilization (%)	Increase in 112 mA/g Utilization (%)	Increase in 179 mA/g Utilization (%)
HGMS	K25	20	22	3.3	4.2
PHGMS	Porous K25	15	4.7	2.4	10

Potential applications of the PHGMS

- Drug delivery
- Nanocatalysis
- Hydrogen storage for fuel cells
- Gases filtration
- MRI contrast agents

Shuyi Li, Lynsa Nguyen, et al. Nanomedicine: Nanotechnology, Biology, and Medicine **6** (2010) 127
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Future work

- Diffusion test
- Load S38 PHGMS in the positive plates
- Determine if the Porous Hollow Glass Microspheres survive in the batteries

Acknowledgment

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