Optimization of Sugar Derived Carbons

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TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

Outline

- **TDA Overview**
- **Sugar Derived Carbons**
  - Capacitance
  - Purity
  - Pore Size Distribution
- **New carbons**
  - Increased purity
- **Improved production methods**
- **Summary**
- **Current Status**

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TDA Overview

TDA Research, Inc. (Wheat Ridge, CO)

- **Founded in 1987**
- **Staff of 70 – mostly chemists and engineers, 60% with advanced degrees**
- **Business plan:**
  - Perform R&D, primarily under government contract
  - Secure intellectual property
    - Small business can retain IP; U.S. Government has royalty-free license to inventions
  - Commercialize technology by:
    - Internal business units
    - Spin-off companies
    - Joint ventures
    - Licensing

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TDA's Facilities

12345-12355 W 52nd Avenue

- 22,000 ft² offices and labs
  - Synthetic Chemistry
  - Catalyst/Sorbent Synthesis/Testing
  - Ceramics Processing
  - Machine and Electronics Shops
  - SEM, TOF Mass Spec

4663 Table Mountain Drive

- 27,000 ft² offices and labs
  - 27 fume hoods
  - Synthetic Chemistry
  - Catalytic Process Development

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Areas of TDA Expertise

- Fullerenes and carbons
- Chemical/biological defense
- Catalysts and Sorbents
- Polymers
- Ceramics
- Aerospace systems

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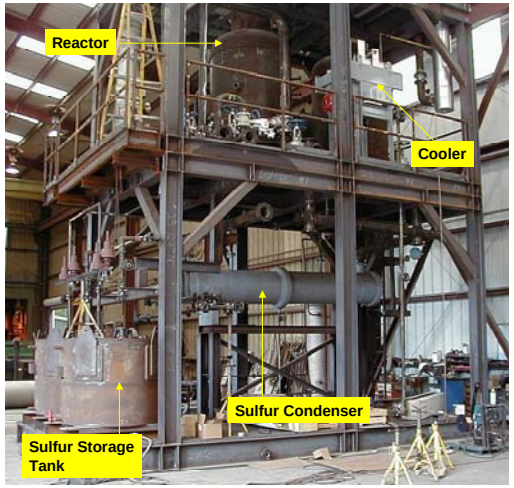
Commercialized Products/Processes

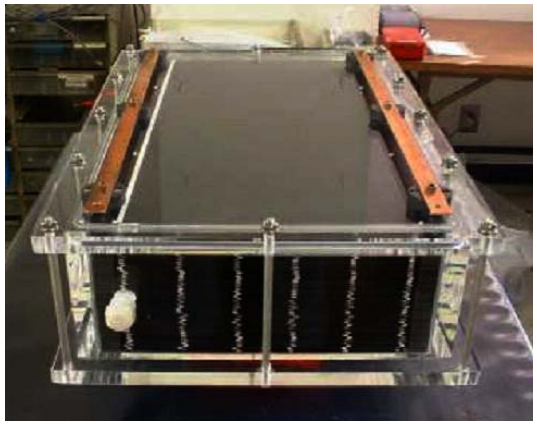
Large Scale Fullerene Production



Partial Oxidation Sulfur Recovery Process

Chemical Heaters

Conducting Polymers



Carbon Electrodes for Water Desalination

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Sugar Derived Carbons

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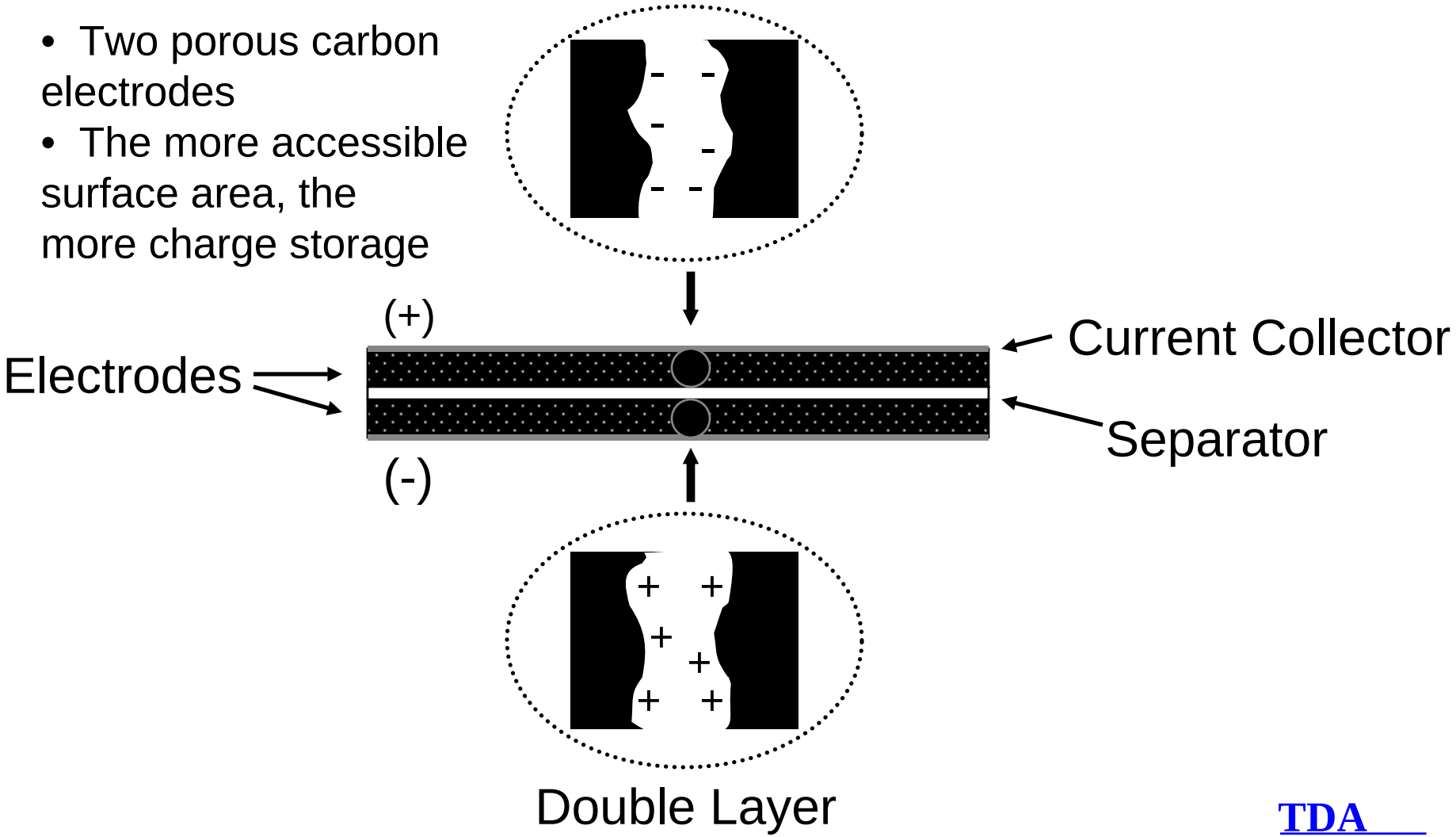
Project Goals

- **Develop improved carbons for symmetric and asymmetric ultracapacitors**
- **Approach:**
  - Optimize the pore structure for aqueous and organic liquid electrolytes
  - Reduce cost of carbons (goal <$10/kg)

Double Layer Capacitance on Porous Carbons

- Two porous carbon electrodes
- The more accessible surface area, the more charge storage



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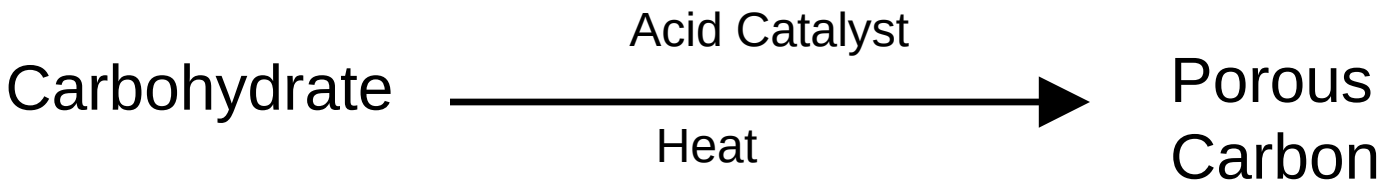
Ideal Pore Size Distribution for Carbon Electrodes

- **Mesopores (2 - 50 nm) for electrolyte access**
- **Micropores (< 2 nm) for high surface area**
- **Benefits:**
- **Increased Capacitance**
  - Pores large enough for the electrolyte to enter yet still maintain high surface areas.
- **Increased Power**
  - Large pores increase rate of ion transport through the electrode resulting in decreased ionic resistance.

Carbon Synthesis from Sugars



- Formulation controls pore size distribution
- Surface area range 300-1000 m^2/g
- For higher surface areas, activate with CO_2 or steam
- Carbohydrates – sucrose, glucose, fructose, cellulose, etc.
- Advantages: very inexpensive and high purity
- Sucrose costs $0.46/kg US, $0.15/kg World
- Phenol costs $1.32/kg

TDA's Carbohydrate-Based Carbons

- **Manufacturing Process**
  - Aqueous sugar/catalyst solution heated in glass cake pans to make a black solid
  - Solid broken up and sifted to make particle sizes suitable for rotary kiln
  - Carbon activated with CO_2
  - Carbon ground and sifted to –325 mesh
- **Production scaled up to multi-kilogram samples**

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Quartz Rotary Kiln

11” diameter
2 kg carbon/run

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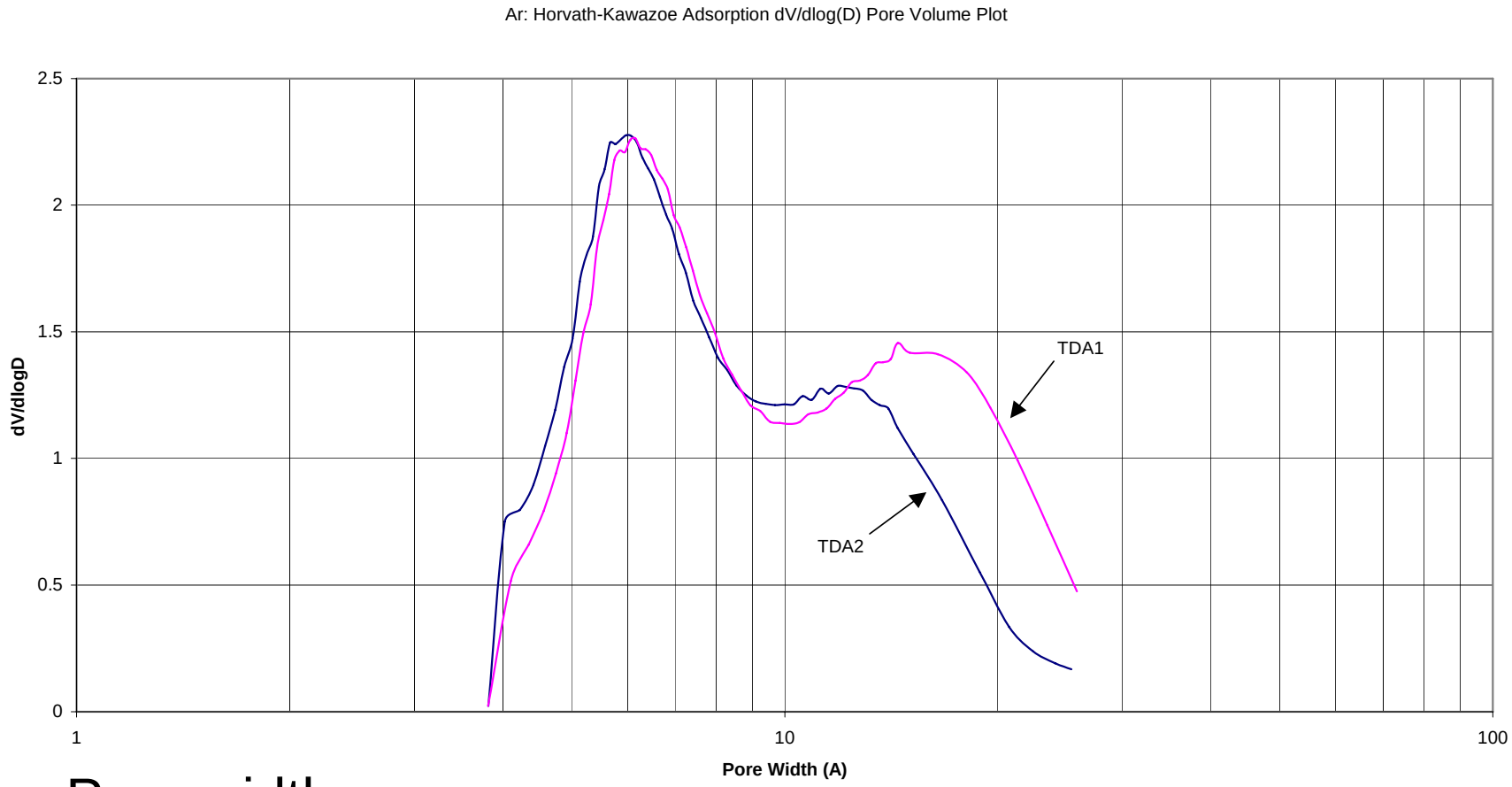
Capacitance (C) Values of TDA's Carbons in Organic Electrolyte (2004)

- **Tested by JME, Inc. (Cleveland, OH)**
- **Electrolyte – 1 M NEt_4BF_4 in DMC/PC**
- **0.001 in. thick separator**
- **Two identical electrodes 0.625 in. diameter, 0.002 in. thick (powders with Teflon binder)**

Sample	Electrode Density (g/cm^3)	ESR (Ω)	Cap. (F/g)	Cap. (F/cc)	RC (sec)
TDA1	0.55	1.327	104	57	0.38
TDA2	0.61	1.123	131	80	0.45

Several tens of kilograms of TDA1 has been sampled to a number of ultracapacitor manufacturers and shows good cycle life and a wide voltage window (2.7 V in ACN)

HK Pore Size Distribution (Ar)



Pore widths:

TDA1 = 0.6 and 1.6 nm

TDA2 = 0.6 and 1.2 nm

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Carbon Impurities

- **The presence of metals and heteroatoms in the carbon can lead to problems such as:**
  - Short cycle life
  - Narrow voltage window
  - High leakage currents
  - Catalyze electrolyte decomposition

Elemental Composition and pH of TDA1

Element		
Carbon	Wt.%	97.17
Hydrogen	Wt.%	0.34
Nitrogen	Wt.%	0.23
Oxygen	Wt.%	1.28
Sulfur	Wt.%	0.35
Ash	Wt.%	<0.05
Calcium	μg/g	32
Chromium	μg/g	<10
Copper	μg/g	<10
Iron	μg/g	<20
Manganese	μg/g	<10
Nickel	μg/g	<10
Potassium	μg/g	146
Silicon	μg/g	65
Sodium	μg/g	22
Zinc	μg/g	<10
Zirconium	μg/g	<10
pH		9.6

Main impurity of concern is sulfur

Source of sulfur is the sulfuric acid catalyst

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Elemental Composition of TDA2

Element		
Carbon	Wt.%	92.28
Hydrogen	Wt.%	0.31
Nitrogen	Wt.%	1.58
Oxygen	Wt.%	2.26
Sulfur	Wt.%	2.75
Ash	Wt.%	0.97

Higher ash and sulfur content than TDA1

Attempts to Remove Sulfur from TDA1 and TDA2 Carbons

- **Water wash of carbon precursor and product**
- **Heat treatment in inert and hydrogen atmospheres**
- **Neither method was successful**

New Carbon TDA3

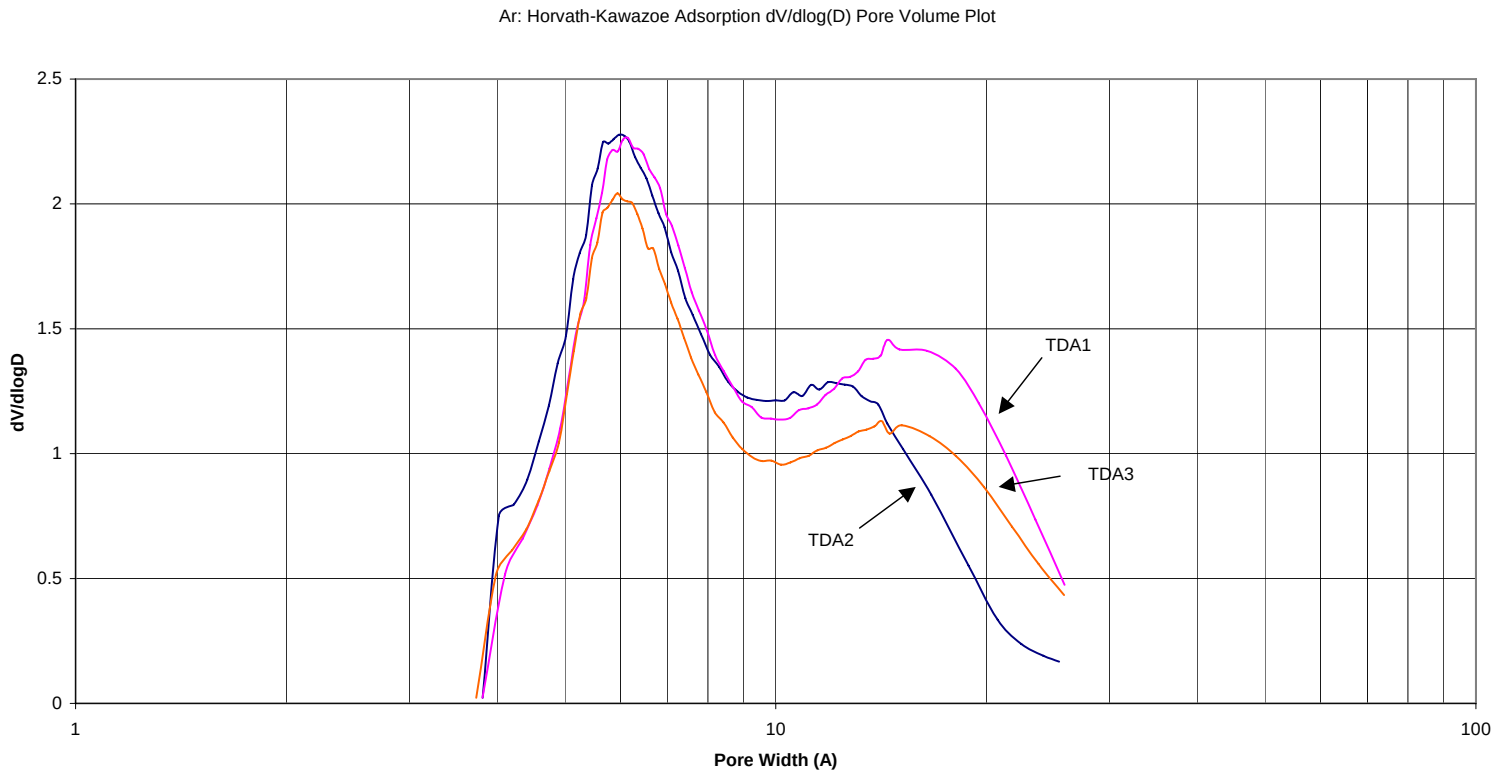
- **Carbon prepared with acid that does not contain sulfur**

Element		
Carbon	Wt.%	97.88
Hydrogen	Wt.%	0.29
Nitrogen	Wt.%	0.19
Oxygen	Wt.%	1.03
Sulfur	Wt.%	0.03
Ash	Wt.%	0.06
pH		6.3

Comparison of TDA3 with Prior Carbons in Organic Electrolyte

Sample	Electrode Density (g/cm^3)	ESR (Ω)	Cap. (F/g)	Cap. (F/cc)	RC (sec)
TDA1	0.55	1.327	104	57	0.38
TDA2	0.61	1.123	131	80	0.45
TDA3	0.56	1.241	93	52	0.33

HK Pore Size Distribution (Ar)



Pore widths:

TDA1 = 0.6 and 1.6 nm

TDA2 = 0.6 and 1.2 nm

TDA3 = 0.6 and 1.5 nm

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Summary of Physical Properties of Carbons

Sample	N_2 BET (cc/g)	N_2 Total Pore Volume (cc/g)	Ar Pore Volume < 2.6 nm (cc/g)	Ar Pore Volume < 2nm (cc/g)
TDA1	2271	1.24	1.08	0.99
TDA2	1992	1.11	0.97	0.94
TDA3	1882	1.16	0.92	0.86

- The lower gravimetric capacitance of TDA3 is likely due to lower surface area and micropore volume

Conclusions

- **Successfully removed sulfur from carbon by changing acid catalyst**
- **Need to optimize pore size distribution to increase gravimetric capacitance**

Improved Production Methods

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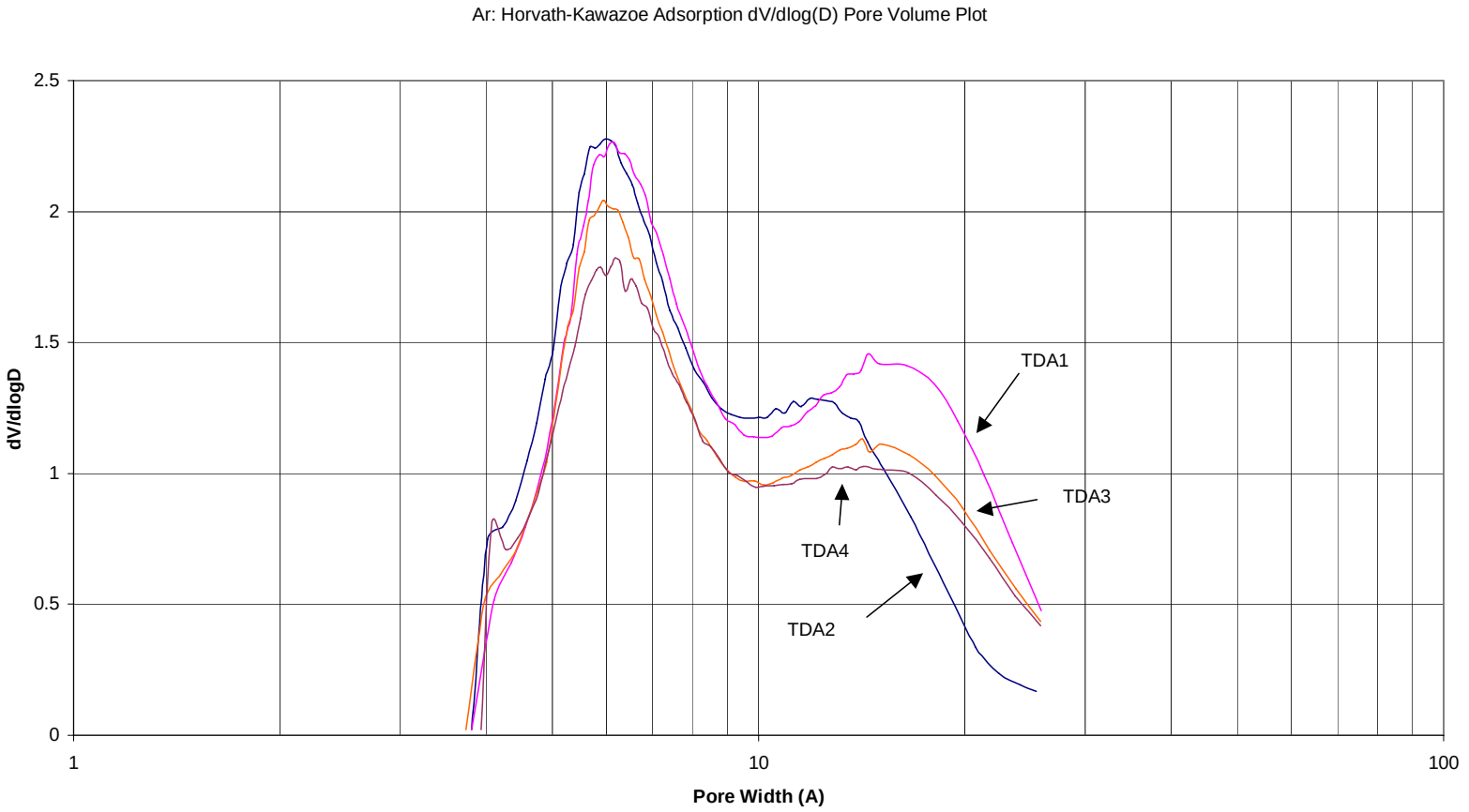
Problems with Old Process (Cake pans)

- **Difficult to scale up**
- **Solid sticks to pans**
- **Not all formulation give suitable material**
- **Considerable material lost to fines**

New Process

- **Aqueous sugar/catalyst solution heated make a fine powder precipitate**
- **Powdered product is filtered and converted into pellets using a screw extruder and binder**
- **Carbon activated with CO_2**
- **Carbon ground and sifted to –325 mesh**
- **Advantages:**
  - Easy to scale-up into continuous process
  - All formulations can be used
  - No loss of material

HK Pore Size Distribution (Ar)



- TDA4 prepared using same formulation as TDA3, but using new powder process method
- Pore size distribution of TDA3 and TDA4 are very similar

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Comparison of TDA4 with Prior Carbons in Organic Electrolyte

Sample	Electrode Density (g/cm^3)	ESR (Ω)	Cap. (F/g)	Cap. (F/cc)	RC (sec)
TDA1	0.55	1.327	104	57	0.38
TDA2	0.61	1.123	131	80	0.45
TDA3	0.56	1.241	93	52	0.33
TDA4	0.70	1.772	96	67	0.60

- TDA4 shows improved volumetric capacitance compared to TDA3
- Improved electrode density is likely due to better packing of precipitated carbon

Summary

- **Elemental analysis of carbons showed that the main impurity was sulfur**
- **Source of impurity was due to sulfuric acid catalyst**
- **Switched acids to remove sulfur**
- **Developed new process to manufacture carbon that is simpler and gives carbons with increased volumetric capacitance**

Current Status

- **Supplying multi-kg samples to ultracapacitor manufacturers for their evaluation**
- **Upgrading facilities to produce large quantities of carbon precursor pellets**
- **Negotiating joint development agreement with major carbon manufacturer with the goal of bringing the carbon from the lab to commercial production**

Acknowledgements

- **DOE I&I program**
- **JME, Inc.**