Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

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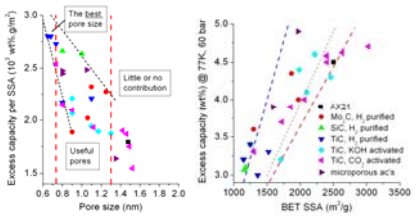
Objectives and Milestones

- Determine the optimal pore size for high pressure, low temperature hydrogen storage.
- Increase volumetric uptake by using bulk samples (eliminate macropores) .
- Demonstrate that the methane storage is possible at room temperature using a similar material system.

Performance Measure	Units	Experimental Condition	2009 Performance Target	2010 Performance Target
Volumetric H_2 and CH_4 storage capacity	g_{H2}/ L	60 bar, 77 K	35	45
	$V(STP)_{CH4}$/ V	35 bar, 273 K	146	180

Excess H_2 capacity normalized to SSA vs. average pore size



Excess capacity normalized to SSA vs. average pore size and excess capacity vs BET SSA

Y. Gogotsi, et al, *Int.J. Hydrogen Energy* (2009)

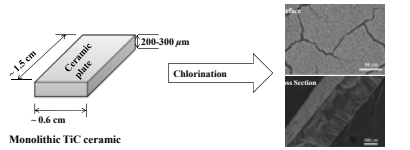
Etching of fully dense ceramic plate

Advantages :

- ✓ Ideal density in the volumetric conversion
- ✓ No macropores
- ✓ Similar to the powder pore structure
- ✓ Controlled microporosity

Limitations:

- ✓ Incomplete reaction at low temperatures
- ✓ Longer chlorination time

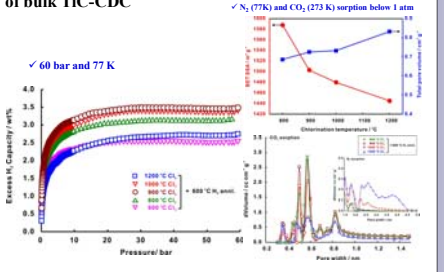


Monolithic TiC ceramic ρ= 5.3 g/cm³ **Bulk TiC-CDC**

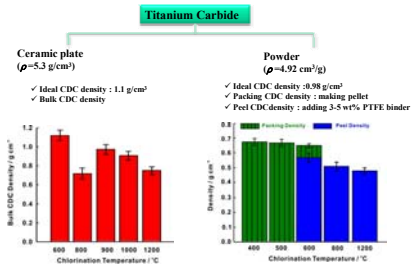
Excess H_2 capacity and porosity of bulk TiC-CDC

✓ N_2 (77K) and CO_2 (273 K) sorption below 1 atm

✓ 60 bar and 77 K



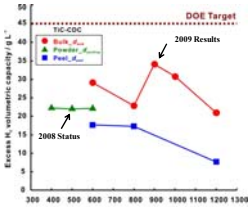
Comparison of various densities



Excess volumetric H_2 capacity

Volumetric capacity

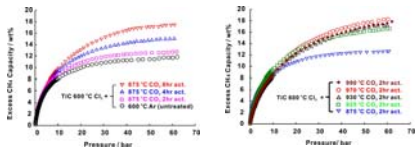
- ✓ Maximum volumetric uptake : ~ 35 g/L at 900 °C Cl_2 of bulk TiC
- ✓ 70 % of the DOE target (45 g H_2/L)



Excess CH_4 capacity of post activated CDC

Physical activation in CO_2

- Activation performed on TiC CDC synthesized at 600 °C Cl_2.
- Maximum CH_4 capacity : 16 wt% at 35 bar and 18.5 wt% at 60 bar.
- CH_4 uptake increases with increasing activation time and temp.



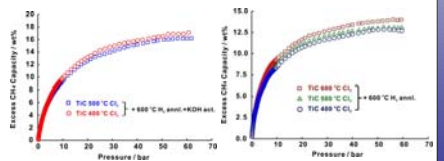
Excess CH_4 uptake measured at 25 °C

S.-H. Yeon, et al, *J. Power Sources*, (2009)

Excess CH_4 capacity of post activated CDC

Chemical activation in KOH (collaboration with Alicante, Spain)

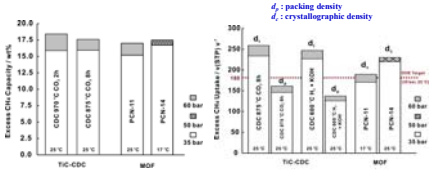
- Maximum CH_4 capacity : 15.5 wt% 35 bar and 16. 8 wt% 60 bar.
- CH_4 uptake increase by 30-40% compared to H_2-annealed CDCs.



✓ Excess CH_4 uptake was measured at 25 °C.

Comparison of excess volumetric and gravimetric CH_4 capacity

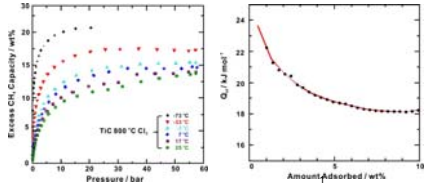
- ✓ Activation performed on TiC-CDC synthesized at 600 °C Cl_2
- ✓ DOE target 180 v(STP)/v at 35 bar and 25 °C



S.-H. Yeon, et al, *J. Power Sources*, (2009)

Methane excess adsorption isotherm

- ✓ TiC CDC synthesized at 800 °C Cl_2 was annealed by NH_3 at 600 °C.
- ✓ The heat of adsorption decreases with increasing gas sorption.
- ✓ The strongest binding energy : ~ 24 kJ/mol



Summary

- Purified CDC's subjected to chemical or physical activation can match or exceed, gravimetric sorption capacity of activated carbons. The key is a careful control of pore size and size distribution, while maximizing SSA.
- Hydrogen uptake results on TiC-CDC obtained at low temperature and high pressure need to be extended to other CDC families, in search of high performance at lower T and P.
- This may be achieved by increasing isosteric heat of adsorption via surface treatment or transition metal doping.

Comparison of Hydrogen Storage of TiC-CDC

Material	Gravimetric H_2 uptake (wt%)	Volumetric H_2 uptake (g/L)	T (K)	P (bar)
Bulk TiC-CDC	3.5	35	77	60
Powder TiC-CDC	3.5	23	77	60

Methane Storage of TiC-CDC Powder Activated by CO_2

Material	Gravimetric H_2 uptake (wt%)	Volumetric H_2 uptake (v(STP)/v)	T (K)	P (bar)
TiC-CDC activated by CO_2	16	146	273	35
	18	161	273	60