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On Effectiveness Factor during Roll-to-Roll Transfer Process for Graphene in Horizontal Low Pressure Chemical Vapor Deposition Annular Plug Flow Reactor

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Graphene

- Graphene is a distinct Allotrope of Carbon
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- Other Allotropes – Fullerenes, C_{60}, Diamond, Graphite, Carbon Nanotubes, CNTs
-
- Unscrolled CNT is graphene. Graphite comprises of graphene layers with interlayer bondind strength of 5.9 $KJ.mol^{-1}$.
-
- Graphene has a unique 2D, two dimensional, hexagonal lattice structure made up of sp^2 hybrized planar sheet of carbon atoms.
-
- Possesses interesting electronic, optical, mechanical and thermal properties.
-
- Interesting applications are expected for SG in the areas of computing , energy and medicine.
-
- EU, European Union, is investing 1 billion euros as funding for ten years in order to explore commercial applications for graphene.
- The Russian initiative is to spend $8.55 billion in order to create nanotech industry by the year 2015.

- Korea ~ $350 million & 7500 patents related to graphene. China, US and South Korea are leading in number of patents acquired in graphene.

- Top industrial participants - IBM, Xerox and Samsung.

- € 10 million is invested in Germany on carbon innovation center.
-
- 100 papers were presented at a APS, American Physical Meeting at Denver, CO in 2007. Nobel Prize was awarded in '10 to A. Geim and Novosolev.

- Prof. R. Ruoff at University of Texas, Austin has rubbed tiny pillars of graphite against a silicon wafer surface causing them to spread out like a deck of cards
-
- Electrons are delocalized in the hexagonal sheet of atoms and move without obstacle
- Chiral, arm chair and puckered morphology of graphenes are possible.

- In order to puncture a graphene sheet with the thinness of saran wrap an elephant balanced on a pencil is needed.

..attributes

- Graphene is a natural substance. It is 200 times stronger than steel and has a tensile strength of 1.5 million psi. International standards have yet to be established for graphene.
- According to recent Lux report the projected market value of graphene by 2018 is $180 million.
- According to the BBC, British Broadcasting Corporation by 2020 the market value of graphene will be $675 million. The Lux report did not include a economically scalable model of fabrication of graphene in their estimates.
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- A number of scalable methods to make graphene is discussed in my book.
- The cost of production of graphene is expected to come down as the technologists move past the learning curve. It costs $60 per square inch of graphene on copper substrate. Expectations are for the costs to come down to $1 per square inch of industrial electronic applications and 10 cents per square inch for use in touch screen displays
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- Applications range from higher capacity electrodes, anti-reflection coatings in solar cells, carbon composites for lighter weight BMWs, panel displays in wireless telephones and laptops, thermal management, cancer treatments, feather-weight HD, high definition televisions, inks, NEMS, . Graphene can be used in study of sequences of RNA and DNA.
-
- von Newmann bottle neck can be obviated by design of novel MLG, magneto logic gates. Bilayer graphene can be used to provide tunable bandgap needed in supercapacitors, LEDS and other applications.

Delocalized Electrons - Resonant

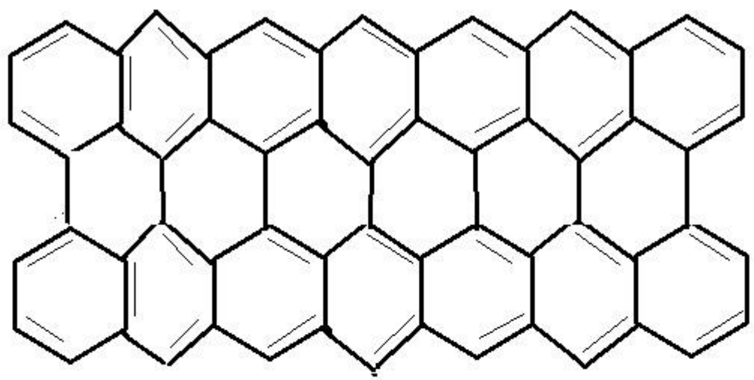
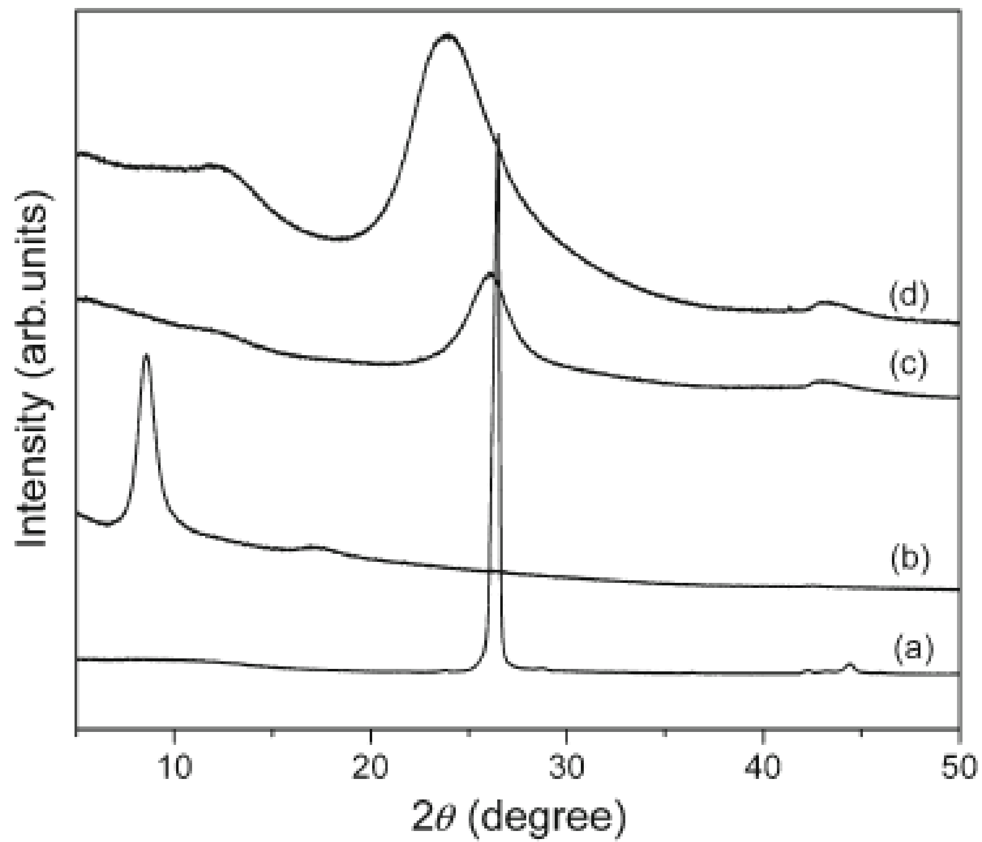


Figure 1.3 **Delocalization of Electrons in P Orbitals in Graphene Monolayer**

XRD Pattern of Graphene



- XRD, x-ray diffraction has been used to obtain the Bravais lattice structures in materials science.
- Graphene can also be characterized using XRD.
- The peak found in graphite broadens in graphene.
- Larger nterlayer spacing d estimates can be used to confirm graphene.
- The graphene formed from different process conditions can be distinguished using the XRD spectra.

Roll-to-Roll Transfer Process – Annular Plug Flow Reactor

- Three Steps

- Adhesion of polymer supports to the graphene on copper foil. Two rollers are used to get the graphene film grown on a copper foil to be attached to a polymer film coated with adhesive film as it passes through;

- Etching of copper layers. Electrochemical reaction with aqueous 0.1 M ammonium persulphate solution $(NH_4)_2S_2O_8$ enables the removal of copper layers and;

- Release of the graphene layer onto a target substrate. Thermal treatment is used to detach the graphene from the polymer support and reattach the film onto a target substrate. This target substrate could have been placed below the copper foil in order to obviate the third step.

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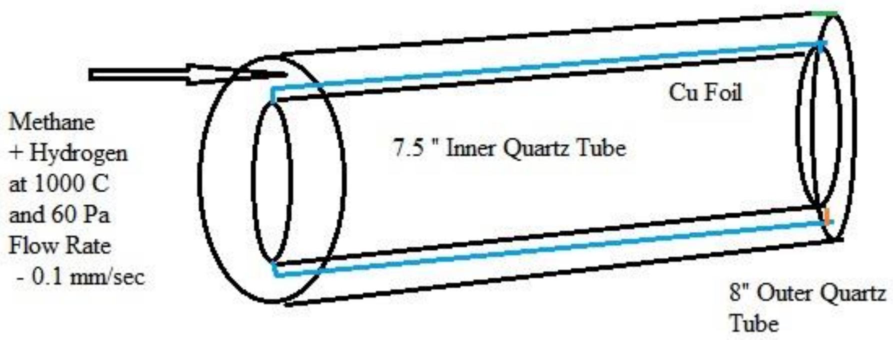
Methane
+ Hydrogen
at 1000 C
and 60 Pa
Flow Rate
- 0.1 mm/sec
Cu Foil
7.5 " Inner Quartz Tube
8" Outer Quartz
Tube

Mechanism of Formation of Graphene on Carbon Foil

- **Dissociation**
- $2CH_4 \rightarrow C_2H_2 + 3H_2 (1)$
- $1000\,^{o}C$
- **Adsorption**
- $C_2H_2 + 2Cu \rightarrow Cu.C_2 + H_2 \quad (2)$
- **Surface Reaction**
- $Cu.C_2 \Leftrightarrow Cu + 2C \quad (3)$

Adsorbtion – Langmuir Isotherm

- [filled sites] + [empty sites] ⇔ [filled sites] (4)

- Sites are subject to chemical equilibrium;
- [bulk solute] + [empty site] ⇔ [filled site] (5)
- $$K = \frac{[filled\_sites]}{[bulk\_solute][empty\_site]}$$ (6)
- $$[filled\_sites] = \frac{K[bulk\_solute][total\_sites]}{1 + K[bulk\_solute]}$$ (7)

- The rate of adsorption can be written as follows;

- Rate of adsorption r” = $\frac{k_0 p_{C_2H_2}}{1 + K' p_{C_2H_2}}$ (8)

Effectiveness Factor

- Effectiveness Factor

$$\eta = \frac{\text{rate\_of\_reaction(actual)}}{\text{rate\_of\_reaction(if\_entire\_interior\_is\_at\_surface\_conditions)}}$$

$$\eta = \frac{2\int \pi D_c [-r''] dD}{\pi D_c^3 \left(-r''_A\right)} = \frac{D_{C_2H_2}\left(\frac{\partial C_{C_2H_2}}{\partial r}\right)_{D=D_c}}{D_c\left(-r''_A\right)}$$

Autocatalytic Reaction – Simultaneous Diffusion in Annular Space of APFR

- Mass Balance on a cylindrical shell in annular space of a APFR of length L (long) and outer radius R and inner radius κR;

$$\frac{1}{r}\frac{\partial (r J_r)}{\partial r} + \frac{\partial C_{C_2H_2}}{\partial t} + k''' C_{C_2H_2} = 0$$

- Method of Separation of Variables
- Obtain Concentration Profile as a Function of Space and Time
- APFR
- Chemical Vapor Deposition of Graphene on Copper Foil
- Branched, Free Radical Mechanism
- Free Radicals will be Neutralized at the Surface
- Surface to Volume Ratio
- Free Radicals makes the Reaction Autocatalytic

Time and Space Conditions

- Initial Condition – 0 concentration of acetylene
- At infinite time the concentration of the acetylene in the entire reactor reaches the maximum value and that r = R.

$$\frac{\partial C_{C_2H_2}}{\partial r} = 0$$

- At r = R, at the wall of the quartz reactor is impervious

$$\frac{\partial C_{C_2H_2}}{\partial r} = 0$$

at r = 0 although the interest is only in the annular space the resulting function has to be symmetric at r = 0. There is no good reason for asymmetry in the radial direction.

Governing Equation

- The governing equation can be obtained by eliminating J_r between governing equation and the damped wave diffusion and relaxation equation. The damped wave diffusion and relaxation equation can be written as follows;

$$J_r = -D_{H_2}\frac{\partial C_{H_2}}{\partial r} - \tau_r \frac{\partial J_r}{\partial t}$$

- Damped Wave Diffusion and Relaxation Equation

$$J_r = -D_{H_2}\frac{\partial C_{H_2}}{\partial r} - \tau_r \frac{\partial J_r}{\partial t}$$

- Eliminate the cross derivative of molar flux J with respect to space and time

....in Concentration

- Governing Equation

$$\tau_r \frac{\partial^2 C_{E1}}{\partial t^2} + (1 + k'' \tau_r)\frac{\partial C_{E1}}{\partial t} = D_{E2}\frac{\partial^2 C_{E1}}{\partial r^2} + \frac{D_{E2}}{r}\frac{\partial C_{E1}}{\partial r} - k'' C_{E1}$$

- Dimensionless form of the equation is obtained

$$u = \left(\frac{C_{E1} - C_s}{C_s}\right); \tau = \frac{t}{\tau_r}; X = \frac{r}{\sqrt{D_{E2}\tau_r}}; k^* = k'' \tau_r$$

$$\frac{\partial^2 u}{\partial \tau^2} + (1 + k^*)\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial X^2} + \frac{1}{X}\frac{\partial u}{\partial X} - k^* u$$

Solution

- The solution is obtained by the method of separation of variables. First the damping term is removed by multiplying the above equation by $e^{n\tau}$. It can be seen that the terms group as W = $ue^{n\tau}$ and the governing equation becomes at n = (1-k*)/2;

$$\frac{\partial^2 W}{\partial \tau^2} - (1+k^*)^2 \frac{W}{16} = \frac{\partial^2 W}{\partial X^2} + \frac{1}{X}\frac{\partial W}{\partial X}$$

- Let W = V(τ) ϕ (X)

$$\phi''(X) + \frac{\phi'(X)}{X} + \lambda^2 \phi(X) = 0$$

$$\frac{V''}{V} = \left(\frac{1+k^*}{2}\right)^2 - \lambda^2$$

Solution

- $\phi = c_1 J_0 (\lambda X) + c_2 Y_0 (\lambda X)$
- It can be seen that $c_2 = 0$ from the symmetry condition that the derivative of the concentration with respect to $r = 0$. Now from the BC at the surface,

$$\frac{\partial u}{\partial X} = 0 = c_1 \frac{\lambda}{\sqrt{D_{C_2H_2}\tau_r}} J_1\left(\frac{\lambda_n R}{\sqrt{D_{C_2H_2}\tau_r}}\right)$$

$$\lambda_n = 3.83\frac{\sqrt{D_{C_2H_2}\tau_r}}{R} + (n-1)$$

Time Domain

- The solution for time domain is the sum of two exponentials. The term containing the positive exponential power exponent will drop out as with increasing time the system may be assumed to reach steady state. At steady state or infinite time W = uexp(τ/2), becomes zero multiplied with infinity. This is in a inderdeterminate form of the fourth kind (Piskunov). This can be shown to go to zero. Thus,

$$V = c_4 e^{-\tau\sqrt{\left(\frac{1+k^*}{2}\right)^2 - \lambda_n^2}}$$

- Infinite Modified Fourier Bessel Series Solution

$$u = \sum_{1}^{\infty} c_n I_0(\lambda_n x) e^{-\tau\left(\frac{1+k^*}{2}\right) - \tau\sqrt{\left(\frac{1+k^*}{2}\right)^2 - \lambda_n^2}}$$

- The c_n can be solved for from the initial condition by using the principle of orthogonality for Bessel functions. At time is zero the LHS And RHS are multiplied by $J_o(\lambda_m X)$. Integration between the limits of 0 and R is performed. When n is not m the integral is zero from the principle of orthogonality. Thus when n = m,
- $c_n = - \int_o^R J_o(\lambda_n X) \quad / \quad \int_o^R J_o^2(\lambda_n X)$
- It can be noted from Eq. [3.191] that when
- $(1 + k^*)^2/4 < \lambda_n^2$
-
- the solution will be periodic with respect to time domain. This can be obtained by using De Movries theorem and obtaining the real part to $\exp(-i\tau \sqrt{(\lambda_n^2 - (1 + k^*)^2/4)})$.

Bifurcated Solution

- For Large Relaxation Times the Concentration of Graphene (Product) will undergo Oscillations.
- $$\tau_r > \frac{(1+k^*)^2 R^2}{587 D_{C_2H_2}}$$
- Estimates of Relaxation Time from Stokes-Einstein Formulation from Chemical Potential (Sharma, 2006)

$$\tau_r = \frac{\rho D_{C_2H_2}}{P}$$

- For Graphene at 5 torr this can be 50 minutes

Shape Limit

- The surface to volume ratio needs to be maintained high. It can be seen that there exist a critical value of R above which the rate at which the free radicals are produced in the reaction is larger than the rate at which it is removed by diffusion. This will lead to a runaway condition in autocatalytic reactions. At the critical value,
-
- $(2R\ h\ \pi)\ \partial u/\ \partial X\ C_s\ D/\sqrt{D\tau_r} = (\pi\ R^2\ h)\ (k'''\ C)$ (3.202)
- or $R_{crit} = 4\ \sqrt{D/k'''}\ J_1\ (R\ \sqrt{(k'''/D)})/J_0(R\ \sqrt{(k'''/D)})$ (3.203)
- Considering the average reaction rate instead,
-
- $R_{crit} = 2\sqrt{D/k'''}\ \ J_1\ (R\ \sqrt{(k'''/D)})$ (3.204)
-

Conclusions

- Graphene can be made in Large Scale
- Annular Plug Flow Reactor
- Simultaneous Diffusion and Reaction of Acetylene in Annular Space Considered
- Damped Wave Diffusion Effects Significant. Relaxation Time ~ 50 minutes
- Governing Equation Solved for by Method of Separtion of Variables
- Infinite Modified Fourier-Bessel Series Solution
- For Large Relaxation Times – Subcritical Oscillations
- Steady State – Shape Factor Effect. Critical Size for R.

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