Tafel based model for understanding fouling and anti-fouling behavior
To explain the four scenarios of the model presented in the earlier chapter, Tafel studies on polyol electrooxidation have been carried out. The catalysts that are used include palladium on multiwall carbon nanotube (Pd-CNT), palladium on octa decyl amine capped multiwall carbon nanotube (Pd-ODA-CNT), platinum on multiwall carbon nanotube (Pt-CNT) and platinum on octa decyl amine capped multiwall carbon nanotube (Pt-ODA-CNT). All these catalysts have been synthesized by a microwave induced reaction and are well characterized. Glycerol electrooxidation reaction (GOR) and ethylene glycol electrooxidation reaction (EGOR) have been studied in alkaline medium with the use of nanocatalysts to explain in detail this electrochemical model. The pictorial mechanism of EGOR and GOR on Pd surface has been well elaborated in Scheme 1.

Scheme 1: Blocking effect of capping agents on electrocatalysis.

The present study is an attempt to understand and evaluate the role of capping agents towards fouling or anti-fouling electrocatalyst surface response. We intend to achieve this by adopting precise experimental controls involving a judicious choice of the catalytic material. This helps to study the blocking or poisoning effects in isolation or in a combination. Towards this end, Tafel plots have been used in similar lines in this study, as in the case of Au-CNT composite that was used to understand scenario 1 (Chapter 5). Pd-CNT is also used to understand scenario 1 of the model while Pd-ODA-CNT composite is used to understand scenario 2. Pt-CNT and Pt-ODA-CNT composites have been used likewise to understand scenario 3 and scenario 4 respectively.
1. **Materials and Methods**

MwCNT with an outer diameter of 20-30nm and 95% purity were bought from Cheap Tubes Inc. Glycerol, Ethylene glycol, Sodium hydroxide, and Perchloric acid chemicals used in this study were of AR grade. All aqueous solutions were prepared using Millipore water having a resistivity of 18.2 MΩ cm.

In the present study, Pd-CNT, Pt-CNT, Pd-ODA-CNT, Pt-ODA-CNT were synthesized by a microwave accelerated reaction system using CEM Mars, fitted with internal temperature and pressure controls. The details of the synthesis are discussed in the experimental methods.

2. **Experimental**

2.1. **Synthesis of carboxylated functionalized multi-walled carbon nanotubes (MwCNT-COOH)**

MwCNT-COOH was synthesized using CEM Mars microwave Accelerated Reaction System with inbuilt temperature and pressure controls. A mixture of conc. H₂SO₄ and HNO₃ was added to pre-weighed amounts of purified MwCNT under microwave conditions for 20 minutes at 140°C. This resulted in functionalization of the nanotube surface predominantly with carboxyl groups, leading to an increased aqueous dispersibility. The resultant solid component was filtered using a 10μm filter membrane, rinsed with water until a neutral pH was achieved. Finally, it was dried at 80°C under vacuum to constant weight.

2.2. **Synthesis of octa decyl amine capped multi-walled carbon nanotubes (MwCNT-ODA)**

MwCNT-COOH was used as the precursor to synthesize organic dispersible MwCNT-ODA. Weighed amounts of MwCNT-COOH was mixed with thionyl chloride and catalytic amounts of dimethyl formamide and subjected to microwave irradiation at around 70°C for 20 minutes. This step resulted in the formation of MwCNT-COCl that was dried under vacuum conditions at room temperature for 12 hours. MwCNT-COCl was treated with octadecyl amine and subjected to microwave irradiation at 120°C for 10 minutes. The product was then filtered and rinsed with hot ethanol and dichloromethane and dried under vacuum conditions at room temperature to yield MwCNT-ODA.

2.3. **Synthesis of Pd-ODA-CNT**

100 mg of MWCNT-ODA was treated with 30 mL of ethanol mixture containing 12.5 mM palladium dichloride (PdCl₂) under microwave conditions at 190°C for 10 minutes. The product was thoroughly filtered, then washed with 0.5 N HCl solution followed by water and dried under vacuum conditions at room temperature for 12 hours.
2.4. Synthesis of Pd-CNT
100mg of CNTs was treated with 12.5 mM PdCl$_2$ ethanol mixture and subjected to microwave radiation at 190°C for 10 minutes. The resultant solid was filtered, washed with 0.5 N HCl, followed by water. The solid was subsequently dried at room temperature in vacuum for 12 hours.

2.5. Electrocatalytic experiments
All electrocatalytic experimentation was performed using a 3 electrode set up consisting of Platinum counter electrode, Ag/AgCl reference electrode and CPE as the working electrode. A carbon paste was prepared by homogeneously mixing 50 mg of graphite powder with 18µl of paraffin oil. The resultant carbon paste was packed into the working electrode and carefully smoothened using a butter paper. The geometrical area of the working electrode was determined to be 0.071 cm$^2$. For the electrochemical studies, 1mg of Pd-CNT was dispersed in 1ml of water to form a homogeneous dispersion of which 5µl of the Pd-CNT dispersion was drop cast on the electrode surface and dried at room temperature. The replicability and high purity conditions of the CPE were confirmed by rinsing it with water and amperometrically cleansing it at 2 different potentials. Firstly, a positive 1.2 V potential was applied followed by a negative -0.4 V potential. This routine procedure ensured the regeneration of the electrode surface before every experimental run. Similarly all the other controls of the experiment were prepared for their final use. All the Tafel plots were obtained by conducting chronoamperometric studies at various selected potentials. All temperature studies were done using an electrochemical double jacketed cell linked to a temperature controller Julabo F 25. All the glycerol electrooxidation experiments were done in a solution consisting 1M glycerol in 0.5M NaOH solution. Similarly, all ethylene glycol (EG) electrooxidation experiments were performed in 0.5M NaOH solution comprising of 1M ethylene glycol.

3. Characterization
The nanocomposites were characterized using SEM equipped with an EDAX, SEM images were obtained using LEO 1530 VP Scanning Electron Microscopy fitted with an energy dispersive X-ray analyzer. FTIR measurements were performed using the KBr pellet method on a Perkin-Elmer Spectrum One instrument.

3.1. SEM
The SEM images of MwCNT, MWCNT-ODA, Pd-CNT, Pd-ODA-CNT, Pt-CNT, Pt ODA-CNT hybrids have been presented in Figure 1a to 1f.
MWCNTs had a diameter between 20-40 nm and length of about 10-30 µm. There was no observable change in the tube morphology after treatment with acid, amidation or even during composite formation, suggesting that there was negligible damage to the tube’s structure. Pd nanoparticles on the MwCNTs surface were seen as bright spots in the SEM images of Pd-CNT as well as Pd-ODA-CNT. The Pt nanoparticles were globular and evenly distributed on the CNT surface in Pt-CNT and Pt-ODA-CNT composites.
3.2. EDAX
The presence of the Pd and Pt metals on the CNT framework was confirmed by the EDAX data shown in Fig. 2a to Fig. 2d.

**Figure 2.** EDAX images of: (a) Pd-CNT (b) Pd-ODA-CNT (c) Pt-CNT (d) Pt-ODA-CNT

3.3. FT-IR
The presence of functional groups in the composites was confirmed by the FT-IR spectroscopy. The FT-IR spectra of MWCNT, MwCNT-COOH, Pd-CNT, MWCNT-ODA, Pd-ODA-CNT, PtCNT and Pt-ODA-CNT composites have been presented in Fig. 3a to Fig. 3g. The carboxylic stretching frequency in MWCNT-COOH was observed at 1716 cm\(^{-1}\). This particular band was clearly absent in the original MWCNT IR spectrum. The 3422 cm\(^{-1}\) O-H band present in MWCNT-COOH spectrum was attributed to the hydroxyl vibrational stretch of the -COOH group, obtained through acid functionalization. The IR peak observed at 1636 cm\(^{-1}\) in ODA-CNT was assigned to the stretching vibrations of the amide group and the sharp peaks at 2921 cm\(^{-1}\) and 2847 cm\(^{-1}\) were assigned to the stretching vibration of the alkyl chain from ODA.
Figure 3. FTIR spectra of: (a) MWCNT (b) MwCNT-COOH (c) Pd-CNT (d) MwCNT-ODA (e) Pd-ODA-CNT (f) Pt-CNT (g) Pt-ODA-CNT.
In all the samples, the peak at 1576 cm\(^{-1}\) was attributed to the C=C stretching of the carbon grid. The presence of new bands at 970 cm\(^{-1}\) and 996 cm\(^{-1}\) in the spectra of the Pd-CNT and Pd-ODA-CNT confirmed the presence of the metals as presented in Fig. 3c and Fig. 3e. The 3422 cm\(^{-1}\) O-H band in MwCNT-COOH was absent in Pt-CNT and Pt-ODA-CNT. This confirmed the anchoring of the metals to the CNT framework by an esterification process in line with previous reports [1].

4. Results and Discussion

4.1. Determination ECSA

CV has been used to calculate the ECSA of Pd-CNT, Pd-ODA-CNT, Pt-CNT and Pt-ODA-CNT in 0.1 N HClO\(_4\) as presented in Fig. 4a to 4d.

**Figure 4.** CV plots to determine electrochemical surface area (true surface area) of: (a) Pd-CNT (b) Pd-ODA-CNT (c) Pt-CNT (d) Pt-ODA-CNT in 0.1N HClO\(_4\); Scan rate 100 mV s\(^{-1}\).
Palladium oxide formation peak during the forward scan was witnessed around 1.2 V. The oxide stripping cathodic peak during the reverse scan was observed around 0.35 V. The charge calculated under this curve during the reverse scan for Pd-CNT and Pd-ODA-CNT was 47.77µC and 48.29µC. The charge density that corresponds to the reduction of palladium oxide monolayer was 424µC cm$^{-2}$ [1]. This charge density was used to calculate the ECSA of Pd-CNT and Pd-ODA-CNT to obtain their ECSA as 0.113 cm$^2$ and 0.114 cm$^2$ respectively. Similarly, the charge associated with the H adsorption peak in case of Pt is 210µC cm$^{-2}$. Using this data, the charge under the H adsorption peak around -0.2V during forward scan for Pt in Pt-CNT and Pt-ODA-CNT was calculated to be 46.59 µC and 40.59 µC. Their corresponding ECSA’s were calculated to be 0.22 cm$^2$ and 0.19 cm$^2$. These ECSA were obtained by drop casting 5µg of catalyst on a geometric area of 0.071 cm$^2$ of the CPE.

4.2. Electrooxidation of glycerol and ethylene glycol on Pd-CNT, Pd-ODA-CNT, Pt-CNT and Pt-ODA-CNT surfaces

GOR and EGOR have been studied in alkaline medium with the use of 4 different catalytic materials. These catalytic materials: Pd-CNT, Pd-ODA-CNT, Pt-CNT and Pt-ODA-CNT have been judiciously chosen to explain each of the scenarios 1, 2, 3, 4 presented in Table 1.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Blocking Effect (BE)</th>
<th>Poisoning Effect (PE)</th>
<th>BE+PE</th>
<th>Tafel Slope Values (TSV) with increasing temperatures</th>
<th>Electrocatalyst Surface Response (ESR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>Decrease</td>
<td>Anti-fouling</td>
</tr>
<tr>
<td>II</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>Increase</td>
<td>Fouling</td>
</tr>
<tr>
<td>III</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>Increase</td>
<td>Fouling</td>
</tr>
<tr>
<td>IV</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>Increase</td>
<td>Fouling</td>
</tr>
</tbody>
</table>

Table 1. Tafel slopes based assessment of electrocatalyst surface response during Glycerol electrooxidation reaction (GOR) and ethylene glycol electrooxidation reaction (EGOR).
The current densities for all the CV plots have been obtained by dividing the currents with the electrochemical surface areas of the catalysts as shown in Fig. 4. The mechanism of EGOR and GOR on these catalytic surfaces has been well elaborated in Scheme 2.

\[
\begin{align*}
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} + 10\text{OH}^- \leftrightarrow \text{COO}^- - \text{COO}^- + 8\text{H}_2\text{O} + 8e^- & (1) \\
\text{CH}_2\text{OH} & \rightarrow \text{CHOH} - \text{CH}_2\text{OH} + 12\text{OH}^- \leftrightarrow \text{COO}^- - \text{CO} - \text{COO}^- + 10\text{H}_2\text{O} + 10e^- & (2) \\
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} + 14\text{OH}^- \leftrightarrow 2\text{CO}_3^{2-} + 10\text{H}_2\text{O} + 10e^- & (3) \\
\text{CH}_2\text{OH} & \rightarrow \text{CHOH} - \text{CH}_2\text{OH} + 20\text{OH}^- \leftrightarrow 3\text{CO}_3^{2-} + 14\text{H}_2\text{O} + 14e^- & (4)
\end{align*}
\]

**Scheme 2. Mechanism of EGOR and GOR on Pd surface [2].**

Comparative CV plots for GOR and EGOR with electrode modifications, using the 4 different catalysts has been presented in Fig. 5.

**Figure 5. CV overlay for GOR and EGOR for Pd and Pt based electrocatalysts; Scan rate 100 mV s\(^{-1}\).**
In the case of GOR as well as EGOR, Pd-CNT has shown nearly 25 fold increase in electroactivity than Pd-ODA-CNT at 0V. Pt-CNT has shown nearly 5 times enhanced electro-activity than Pt-ODA-CNT at the same potential for GOR and 3 times more for EGOR.

4.3. Electrocatalysts stability study: 200 cycles GOR and EGOR CV

A 200 CV study has highlighted the stability of the electrocatalysts towards fouling or anti-fouling electrocatalyst surface response (ESR). The 200 cycles study for GOR has been presented in Fig. 6 and for EGOR in Fig. 7. The current densities ($j$) have remained similar for Pd-CNT before and after 200 CVs for GOR and even slightly increased in the case of EGOR highlighting the anti-fouling ESR of a spot-free catalyst. On the other hand, Pd-ODA-CNT has shown a significant decrease in the $j$ value after 200 CVs for both GOR and EGOR.

![Graphs showing 200 cycles stability study for GOR and EGOR](image)

**Figure 6.** 200 cycles stability study using CV for GOR; Scan rate 100 mV s$^{-1}$
This emphasizes the non-availability of the catalyst surface active sites in the case of capped electrocatalysts due to the accumulation of carbonaceous intermediates, generated during the course of several continuous CVs. This in turn implies that ODA, used as the capping agent, in the case of Pd-ODA-CNT (Scenario 2) is prone to intermediate accumulation. Its blocking effect on the intermediates, results in fouling ESR. We hence strongly believe that the capping agents that confine the size and shape of nanoparticles and nanostructures also restrict reactant approach and intermediate desorption from the catalyst surface during the electrooxidation reaction, leading to excessive fouling due to intermediate accumulation.

Similarly, Pt-CNT and Pt-ODA-CNT have shown a drastic decrease in current densities during a 200 cycle study owing to surface fouling for GOR and EGOR. In the case of Pt-CNT (Scenario 3), electrode fouling is on account of poisoning effect, surface poisoning of the metal by...
covalent binding of the intermediates. The electrode fouling in the case of Pt-ODA-CNT (Scenario 4) is due to a combination of blocking and poisoning effects owing to the presence of capping agents and the intermediates that are covalently bound to the Pt catalyst surface. This study highlights that poisoning effect is a capping agent independent phenomenon, unlike blocking effect.

4.4. Temperature dependent study of Tafel plots

Importantly, we present the use of Tafel slope values (TSV) that are plots of polarization, to monitor and understand ESR. With regard to the electrooxidation of alcohols, Tafel plots are complex due to the adsorption of the intermediate carbonaceous impurities causing surface fouling and catalytic inhibition [1]. This in turn results in nonlinearity of the Tafel slope during electrooxidation. The fouling of the electrode surface increases with increasing temperature and the Tafel slope thereby increases [3]. All the nanoparticles and nanostructures with capping agents, till date, have shown an increase in Tafel slope behaviour with increasing temperature [1, 3]. We speculate that on a spot-free surface, no accumulation of these intermediates happen on account of the absence of capping agents, increasing the ESR. All the Tafel plots of all the catalyst for both GOR and EGOR have been presented in the Fig. 8 to Fig. 15.
Figure 8. Tafel plots of Pd-CNT for GOR at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C.
Figure 9. Tafel plots of Pd-CNT for EGOR at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C.
Figure 10. Tafel plots of Pd-ODA-CNT for GOR at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C.
Figure 11. Tafel plots of Pd-ODA-CNT for EGOR at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C.
Figure 12. Tafel plots of Pt-CNT for GOR at different temperatures: (a) 10° C, (b) 20° C, (c) 30° C, (d) 40° C, (e) 50° C.
Figure 13. Tafel plots of Pt-CNT for EGOR at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C.
Figure 14. Tafel plots of Pt-ODA-CNT for GOR at different temperatures: (a) 10° C, (b) 20° C, (c) 30° C, (d) 40° C, (e) 50° C.
Figure 15. Tafel plots of Pt-ODA-CNT for EGOR at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C.

In this chapter, Pd-CNT devoid of any capping agent has shown a decreasing TSV trend for both GOR and EGOR, unlike Pd-ODA-CNT as presented in Table 2 confirming blocking effect due to ODA presence.
### Table 2. Tafel slope values for GOR and EGOR with Pd based electrocatalysts (all slope values are in the units of mV \text{dec}^{-1}).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pd-CNT</th>
<th>Pd-ODA-CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOR</td>
<td>EGOR</td>
<td>GOR</td>
</tr>
<tr>
<td>10</td>
<td>140.24</td>
<td>135.83</td>
</tr>
<tr>
<td>20</td>
<td>140.95</td>
<td>132.08</td>
</tr>
<tr>
<td>30</td>
<td>131.77</td>
<td>129.38</td>
</tr>
<tr>
<td>40</td>
<td>125.75</td>
<td>102.95</td>
</tr>
<tr>
<td>50</td>
<td>117.90</td>
<td>94.64</td>
</tr>
</tbody>
</table>

### Table 3. Tafel slope values for GOR and EGOR with Pt based electrocatalysts (all slope values are in the units of mV \text{dec}^{-1}).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pt-CNT</th>
<th>Pt-ODA-CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOR</td>
<td>EGOR</td>
<td>EGOR</td>
</tr>
<tr>
<td></td>
<td>(Slope1)</td>
<td>(Slope2)</td>
</tr>
<tr>
<td>10</td>
<td>242.32</td>
<td>93.46</td>
</tr>
<tr>
<td>20</td>
<td>261.05</td>
<td>123.57</td>
</tr>
<tr>
<td>30</td>
<td>293.97</td>
<td>110.27</td>
</tr>
<tr>
<td>40</td>
<td>342.15</td>
<td>160.27</td>
</tr>
<tr>
<td>50</td>
<td>360.13</td>
<td>165.57</td>
</tr>
</tbody>
</table>

Despite the absence of capping agent, Pt-CNT has shown TSV increase with increasing temperature due to surface poisoning effect. This also corroborates with the 200 cycle study, that highlights poisoning effect is independent of blocking effect. In both Pt-CNT and Pt-ODA-CNT, the TSV increases with increasing temperatures, but the magnitude of TSV increase in Pt-ODA-CNT is larger than Pt-CNT owing to a combination of blocking and poisoning effect as seen in Table 2.
4.5. Temperature dependent study of Arrhenius plots

Interestingly, the Arrhenius plots obtained from the chrono-amperometric data have also validated our results. The activation energy ($E_a$) from the conventional Arrhenius formula is as shown in Eq. 1.

$$k(T) = A e^{-E_a/RT} \quad \text{Eq. 1}$$

$k(T)$ is the rate constant, $A$ is the pre-exponential factor, $T$ is the temperature, $R$ is the gas constant. The $E_a$ value has been obtained from current density values, at different potentials, from varying temperatures using the equation Eq. 2.

$$E_a = R \left( \ln \frac{I_o}{d} \right) / d (1/T) \quad \text{Eq. 2}$$

The apparent $E_a$ has been calculated from the slopes of Arrhenius plot for all the experimental controls (where slope = $-E_a/2.303R$). The $E_a$ value for Pd-CNT is 26.43 kJ mol$^{-1}$, whereas for Pd-ODA-CNT it is 28.08 kJ mol$^{-1}$ for GOR (Fig. 16). The $E_a$ value in case of EGOR for Pd-CNT is 15.98 kJ mol$^{-1}$, whereas, for Pd-ODA-CNT it is 17.79 kJ mol$^{-1}$ as shown in Fig. 16.

The requirement of additional $E_a$ on moving from Pd-CNT to Pd-ODA-CNT in both GOR and EGOR is due to blocking effect associated with the presence of ODA in the case of Pd-ODA-CNT.
Figure 16. Arrhenius plots of Pd based composites for electrooxidation of polyols.
Figure 17. Arrhenius plots Pt based composites for electrooxidation of polyols.

The $E_a$ values for Pt-ODA-CNT is quite high than Pt-CNT as shown in Fig. 17 for both GOR and EGOR. This is due to the combination of blocking and poisoning effects. These results are in line with our understanding of capping agent based fouling behaviour vis-à-vis spot-free electrocatalysis. The spot-free catalysts, however, tend to aggregate over a period of time. This is prevented when they are supported on high surface area substrates such as CNT, as planned in the current study.

5. Conclusions

- We present an assessment of ESR using a Tafel slope based approach that helps understand the fouling role played by capping agents and reaction intermediates. It is worth mentioning here that this has been the first time 4 different electrocatalysts: Pd-CNT, Pd-ODA-CNT, Pt-CNT and Pt-ODA-CNT coupled with TSV with increasing temperatures have been used to understand ESR, using blocking effect, poisoning effect and their combination.
• This study opens the door to predict and monitor intermediates and capping agents based fouling or anti-fouling ESR in electro oxidation reactions.

REFERENCE


