Corrosion Behaviour for SmBa$_2$Cu$_3$O$_{7-\delta}$ Phase containing nanomaterials
Outline/Agenda

• Introduction
• Work Plan
• Materials and Methods
• Results and Discussion
• Conclusion
• Introduction

• Work Plan

• Materials and Methods

• Results and Discussion

• Conclusions
Corrosion is the deterioration of a material due to its reaction with an aggressive environment.

1960, corrosion was restricted to metals and their alloys.

All types of natural and man-made materials including biomaterials and nanomaterials.

Importance of Studying Corrosion

- Safety
- Economic factor
- Conservation of material
**Types of Corrosion**

**Uniform**
Defined as uniform thinning of a metal without any localized attack.

**Intergranular**
Localized attack on the grain boundaries of a metal.

**Galvanic**
Occurs when two metals with different electrochemical potentials are immersed in a corrosive electrolyte.

**Crevice**
Caused by the existence of gaps, between adjacent surfaces.

**Pitting**
Localized attack of a metal surface due to corroding of small areas.

**Fretting**
Occurs due to a small motion between the materials.
Corrosion Control

Substances which can **retard corrosion** when added in small amounts.

- **Inhibitors**
  
  Achieved by supplying an external **negative current** to the **corroding metal**.

- **Cathodic Protection**
  
  Relatively close in the **galvanic** series.

- **Materials Selection**
**Zero resistivity**

At $T_c$, the resistance drops suddenly to an unmeasurable small value. The material undergoes a phase transition from a **normal state** to a **superconducting state at $T_c$**.

**Perfect diamagnetism**

The **expulsion of a magnetic field** from a superconductor during its transition to the superconducting state and occurs only if the magnetic field is relatively small.
Superconductivity

Defined as a rapid disappearance of electrical resistance in a substance when it is cooled below a certain temperature, called the superconducting transition temperature, $T_c$.

The superconducting state is mainly marked by two most remarkable properties.

- Zero resistivity
- Perfect diamagnetism
The superconducting state is defined by three important factors which depend on the material.

Maintaining the superconducting state requires that:

- **Magnetic field**
- **Current density**
- **Temperature**

remain **below the critical values**.
Superconductors are currently used in several domains including:

• Medical diagnosis (MRI-NMR)

• Power stations

• Electronics chips

• Generators and marine motors

• Maglev trains

Most of the studies on these materials concern their mechanical, electric and magnetic properties that made them the promising candidates for technological applications.

Studying the electrochemical corrosion behaviour of superconductors is a need to preserve their superconductivity properties.
Work Plan

Preparation of Mn$_2$O$_3$ nanoparticles using Co-precipitation technique.

Preparation of SmBa$_2$Cu$_3$O$_{7-\delta}$ superconducting phase free from and containing (Mn$_2$O$_3$)$_x$ using solid-state technique.

Characterization of the prepared nanomaterials and superconductors.
Work Plan

Examination of the effect of incorporation of Mn$_2$O$_3$ nanomaterials on the mechanical properties of the prepared superconductors.

Investigation of the electrochemical behaviour of Steel in acidic media in presence of Mn$_2$O$_3$ nanoparticles.

Studying the effect of incorporation of these nanoparticles on the corrosion behaviour of the prepared superconductors.
Materials and Methods
Materials for Nanoparticles Preparation

Manganese(II) chloride tetrahydrate MnCl$_2$·4H$_2$O
(3.5 < pH < 6)

Sodium Hydroxide NaOH

Ethylenediamine tetraacetic acid EDTA
Materials for Superconductor phase Preparation

- Samarium Oxide $\text{Sm}_2\text{O}_3$
- Barium Carbonate $\text{BaCO}_3$
- Cupric Oxide $\text{CuO}$
- Manganese Oxide $\text{Mn}_2\text{O}_3$
Co-precipitation method for nanoparticles preparation

Dissolution of starting materials into distilled water.

Stirring at room temperature for 30 minutes.

Addition of 4.0 M NaOH to fix the pH.

Heating at 70 °C for 2 h.

Filtration and washing.

Drying at 90 °C for 16 h.

Calcination at 550 °C for 6 h.

Final Product
Solid-State method for Sm-123 superconductor preparation

**Mixing, and grinding of powders**

**Sieving process**

**Heating at 930°C for 24 hours**

**Annealing treatment**

24 h

24 h

7 h 16 min

10 h under flow of Oxygen

2.3 mm under flow of Oxygen

**Resultant superconductor discs**

**Pressing at high pressure**

**Final superconductor discs**
Samples Characterization

X-Ray Diffraction powder (XRD)

Transmission Electron Microscopy (TEM)

Scanning Electron Microscopy (SEM)

Energy Dispersive X-ray spectroscopy (EDX)
Fourier Transform Infrared spectroscopy (FTIR)

RAMAN spectroscopy

Ultra-violet Spectroscopy (UV)

Thermal analysis gravimetry (TGA)
Samples Characterization

Vickers Microhardness

Electrical resistivity measurements
Electrochemical Techniques

Electrochemical impedance spectroscopy

Potentiodynamic Polarization Measurements
1. Physical Properties of Mn$_2$O$_3$ nanoparticles synthesized by co-precipitation method at different pH values.
1.1. X-ray Diffraction Measurements (XRD)

Cubic structure for Mn$_2$O$_3$ nanoparticles.

Figure 1.1. X-ray diffraction patterns for Mn$_2$O$_3$ nanoparticle synthesized by co-precipitation method at different pH.
### Table 1.1. Particle size of Mn$_2$O$_3$ nanoparticles synthesized at different pH

<table>
<thead>
<tr>
<th>hkl</th>
<th>pH 10</th>
<th>pH 11</th>
<th>pH 12</th>
<th>pH 13</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (2Ѳ)</td>
<td>Particle Size (nm)</td>
<td>Position (2Ѳ)</td>
<td>Particle Size (nm)</td>
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<tr>
<td>211</td>
<td>23.36137</td>
<td>165</td>
<td>23.1528</td>
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<td>222</td>
<td>33.16778</td>
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<td>65.93816</td>
<td>76.2</td>
<td>65.76458</td>
<td>104.6</td>
</tr>
</tbody>
</table>

**Average particle size (nm)**

- pH 10: 110.48
- pH 11: 106.81
- pH 12: 77.01
- pH 13: 65.91

**Crystalline size as pH**
1.2. Transmission Electron Microscopy

Cubic shape for Mn$_2$O$_3$ nanoparticles

pH

Crystalline size

Figure 1.2. TEM images of Mn$_2$O$_3$ nanoparticles synthesized by co-precipitation method at different pH.
1.3. *Energy Dispersive X-ray analysis*

Figure 1.3. EDX spectra of Mn₂O₃ nanoparticles synthesized by co-precipitation method with different pH values.
### 1.3. Energy Dispersive X-ray analysis

Table 1.2. Elemental composition of Mn$_2$O$_3$ nanoparticles synthesized by co-precipitation method at different pH

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 10</td>
</tr>
<tr>
<td>O (K)</td>
<td>49.753</td>
</tr>
<tr>
<td>Mn (K)</td>
<td>50.217</td>
</tr>
</tbody>
</table>

The oxygen content decreases with pH.

Manganese content is increased with increasing pH.
TGA curves show a weight loss at 712°C. This peak can be attributed to the thermal decomposition of Mn₂O₃ as follows:

$$6\text{Mn}_2\text{O}_3 \rightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2$$

Figure 1.4. TGA graphs of Mn₂O₃ nanoparticles synthesized by co-precipitation method at different pH.
1.5. **FTIR Spectra Analysis**

Stretching and bending vibrations of the OH group

Stretching vibration of Mn-O and Mn-O-Mn bonds during the formation of Mn$_2$O$_3$ nanoparticles.

Figure 1.5. FTIR spectra of Mn$_2$O$_3$ synthesized by co-precipitation method at different pH.
1.6. Ultraviolet-Absorption Spectroscopy

The absorption peaks of Mn$_2$O$_3$ nanoparticles show a shift to the lower wavelength.

Additional confirmation of decrease in particle size with increasing pH.

Mn$_2$O$_3$ nanoparticles could be used in solar cells and photo-catalysts due to their very high absorbance in the visible range.

Figure 1.6. UV-Vis spectrum of Mn$_2$O$_3$ with respect to the pH values.
Two weak phonon bands are shown at about 280 and 480 cm$^{-1}$, respectively, can be related to Mn–O bending vibrations and to the symmetric vibration $v_5$(Mn–O), respectively. A strong phonon band at 640 cm$^{-1}$ was found and can be attributed to $v_1$(Mn–O).
2. Effect of the incorporation of Mn$_2$O$_3$ nanoparticles on the mechanical properties of Sm-123 phase superconductors.
2.1. X-ray Diffraction Measurements (XRD)

- Orthorhombic symmetry for SmBa$_2$Cu$_3$O$_{7-\delta}$ phase superconductor.
- No phase transition from orthorhombic to tetragonal is detected, indicating that Mn$_2$O$_3$ nanoparticle acts only at the boundaries.

![X-ray diffraction patterns](image)

Figure 2.1. X-ray diffraction patterns for Sm-123 phase superconductors in the absence and presence of different Mn$_2$O$_3$ nanoparticles percentages.
This result is confirmed by the values of lattice parameters (a, b and c)

\[
\begin{align*}
\text{a (Å) } &= 3.820 \pm 0.004 \\
\text{b (Å) } &= 3.878 \pm 0.005 \\
\text{c (Å) } &= 11.533 \pm 0.003.
\end{align*}
\]

The same values for both pure and added samples.

Table 2.1. Lattice parameters for Sm-123 samples free from and containing different percentages of Mn$_2$O$_3$ nanoparticles.
2.2. *SEM Measurements*

(a): x=0.00 wt.%  
(b): x=0.02 wt.%  
(c): x=0.08 wt.%

Figure 2.2. SEM images of \((\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}\) phase superconductors.

The shape of the pure sample does not change due to the nano-addition.

\(\text{Mn}_2\text{O}_3\) nanoparticle does not penetrate inside the crystal set and sticks as adhering material to the surface of superconductor phase.
2.3. **EDX Analysis**

![EDX spectra](image)

(a): $x=0.00$ wt.

(b): $x=0.02$ wt.

(c): $x=0.08$ wt.

The existence of Mn element is detected in the sample added with the highest percentage.

The position of Cu, Sm, Ba and O peaks does not change after the addition of Mn$_2$O$_3$ nanoparticles.

*Figure 2.3. EDX spectrum of $(\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase superconductors.*
2.5. Resistivity measurements

A metallic-like behavior in the normal state succeed by superconducting transition at the $T_c$.

Figure 2.5. Electrical resistivity versus temperature for ($\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The variation of $\rho/\rho_T$ vs. temperature is shown in the inset.
2.5. Resistivity measurements

The increase of $T_c$ could be explained by the improvement in the intergrain connectivity.

The lowest value of $\Delta T$ is related to the enhancement of the phase formation due to the homogenous distribution of $\text{Mn}_2\text{O}_3$ nanoparticles on the superconductor surface material.
2.6. **Mechanical Properties of Sm-123 phase superconductors**

The values of $H_v$ decreases non-linearly as the applied load increases, showing a **load dependent regime** at low applied load $F$.

Load independent regime (**plateau region**) at higher loads.

Figure 2.6. The variation of apparent $H_v$ at different applied loads for $(\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase superconductor.
The analysis of the normal Indentation Size Effect (ISE) behavior and the estimation of the true microhardness value could be explained by different models.

Meyer's law

$$F = A d^n$$

- $F$: applied load
- $d$: indentation diagonal length
- $n$ is the Meyer number, indication for the indentation size effect trend
- $A$ is the standard microhardness constant.

Figure 2.7. The variation of $\ln(F)$ versus $\ln(d)$ for $(\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7.5-\delta}$ samples with different values of $x$. 
Table 2.3. Microhardness results of different models for \((\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}\)

<table>
<thead>
<tr>
<th>(x)</th>
<th>(H_v) (Gpa) plateau region</th>
<th>Meyer (n) (N/(\mu)m(^2))</th>
<th>Meyer (A) (N/((\mu)m(^2)))</th>
<th>Meyer (A_1) (N/(\mu)m)</th>
<th>HK (W) (N)</th>
<th>HK (H_{HK}) (Gpa)</th>
<th>MPSR (\alpha_2) (N/((\mu)m))</th>
<th>MPSR (\alpha_3) (N/((\mu)m(^2)))</th>
<th>MPSR (\alpha_4) (N/((\mu)m(^2)))</th>
<th>MPSR (H_{MPSR}) (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.126</td>
<td>1.514</td>
<td>0.013</td>
<td>0.0011</td>
<td>0.634</td>
<td>3.365</td>
<td>0.0306</td>
<td>0.0355</td>
<td>0.0011</td>
<td>3.1245</td>
</tr>
<tr>
<td>0.02</td>
<td>4.07</td>
<td>1.526</td>
<td>0.014</td>
<td>0.0017</td>
<td>0.935</td>
<td>3.513</td>
<td>-0.6872</td>
<td>0.1034</td>
<td>0.0005</td>
<td>4.2027</td>
</tr>
<tr>
<td>0.04</td>
<td>3.58</td>
<td>1.582</td>
<td>0.011</td>
<td>0.0013</td>
<td>0.780</td>
<td>3.496</td>
<td>-0.5152</td>
<td>0.0795</td>
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<td>4.6052</td>
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<tr>
<td>0.06</td>
<td>2.845</td>
<td>1.560</td>
<td>0.014</td>
<td>0.0011</td>
<td>0.898</td>
<td>2.680</td>
<td>-0.3671</td>
<td>0.0707</td>
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<td>2.1912</td>
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<td>0.08</td>
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<td>2.488</td>
<td>-0.4783</td>
<td>0.0699</td>
<td>0.0005</td>
<td>2.098</td>
</tr>
</tbody>
</table>

**Meyer index** value less than 2 indicating the normal ISE. The values of \(A\) are very small, comparing to the ceramic materials.

Meyer’s law can explain the ISE behavior, but it can't determine the true microhardness.
Revealed the existence of a minimum applied test load, \( W \), necessary to initiate plastic deformation

\[
F - W = A_1 d^2
\]

where \( A_1 \) is the load independent microhardness constant.

Hays Kendall load-independent microhardness \( H_{HK} \), can be as follow:

\[
H_{HK} = 1854.4 \times A_1
\]
Table 2.3. Microhardness results of different models for \((\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}\)

<table>
<thead>
<tr>
<th>x</th>
<th>(H_v) (Gpa) plateau region</th>
<th>Meyer</th>
<th>HK</th>
<th>MPSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n) ((\text{N}/\mu\text{m}^2))</td>
<td>(A) ((\text{N}/(\mu\text{m}^2)))</td>
<td>(A_1) ((\text{N}))</td>
<td>(W) ((\text{Gpa}))</td>
</tr>
<tr>
<td>0.00</td>
<td>3.126</td>
<td>1.514</td>
<td>0.013</td>
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<td>0.0010</td>
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</table>

The parameter \(A_1\) ↑ up to 0.02, then it ↓ with further addition, confirming the load-independent microhardness values.

Positive values of \(W\) → the creation of both elastic and plastic deformation due to the sufficient applied load.
Modified Proportional Specimen Resistance (MPSR) model

The load dependence of the indentation is given by the following equation:

$$ F = \alpha_1 + \alpha_2 d + \alpha_3 d^2 $$

- $\alpha_1$ corresponds to the minimum applied load to produce an indentation.
- $\alpha_2$ and $\alpha_3$ are related to energy dissipated in creating a new surface of unit area

$H_{MPSR}$ is a measure of the load independent microhardness

$$ H_{MPSR} = 1854.4 \times \frac{(\alpha_1 + \alpha_2 d + \alpha_3 d^2)}{d^2} $$

Figure 2.9. The variation of $(F)$ as function of $(d)$ for $(\text{Mn}_2\text{O}_3)\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$
Table 2.3. Microhardness results of different models for \((\text{Mn}_2\text{O}_3)_x\) \(\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}\)

<table>
<thead>
<tr>
<th>(x)</th>
<th>(H_v) ((\text{Gpa})) &lt;br&gt;plateau region</th>
<th>Meyer (n) ((\text{N}/\mu\text{m}^2))</th>
<th>(A) ((\text{N}/(\mu\text{m}^2)))</th>
<th>(A_1) ((\text{N}))</th>
<th>HK (W) ((\text{Gpa}))</th>
<th>(\alpha_2) ((\text{N}/\mu\text{m}))</th>
<th>(\alpha_3) ((\text{N}/(\mu\text{m}^2)))</th>
<th>(\alpha_4) ((\text{N}/(\mu\text{m}^2)))</th>
<th>MPSR (H_{\text{MPSR}}) ((\text{Gpa}))</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0013</td>
<td>0.780</td>
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<td>2.488</td>
<td>-0.4783</td>
<td>0.0699</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

The analysis data of these models show that the experimental true microhardness values, for all the samples, are close to those obtained from the HK model.

Hays and Kendall is the best model to study the microhardness of \((\text{Mn}_2\text{O}_3)_x\) \(\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}\).
The Vickers indentation can be used to evaluate critical mechanical parameters such as

- Elastic modulus \((E)\)
- Yield strength \((Y)\)
- Fracture toughness \(K_f\)
- Brittle index \(B_i\).

Table 2.4 displays the values of \(Y, E, K_f\) and \(B_i\) for \((\text{Mn}_2\text{O}_3)_x\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}\) with \((0.00 \leq x \leq 0.08\) wt.\%\).
The tabulated data show an apparent increase for $E$ (GPa) and $Y$ (GPa) with increasing nano-additions from 0.00 to 0.02 wt%.

This behavior can be attributed to the healing of voids and resulted in increase the microhardness.
(\(K_f\)), and (\(B_i\)) for samples increase with the increase of \(\text{Mn}_2\text{O}_3\) nano-addition up to \(x = 0.02\) wt%.

This increase can be related to an **increased Sm-123 grain growth**.
3. Electrochemical corrosion behavior of mild steel in acidic media in the presence of Mn$_2$O$_3$ nanoparticles.
3. 1. Effect of concentration
3.3.1. Electrochemical Impedance Spectroscopy

![Nyquist Impedance Plots](image)

The **diameter** of the obtained **semicircles**, which are directly proportional to the charge transfer resistance and inversely to the corrosion rate:

- **Increases** with increasing \( \text{Mn}_2\text{O}_3 \) nanoparticles concentration up to **20 ppm**
- **Decreases** for further additions.

Figure 3.1. Nyquist impedance plots for steel in 0.5 M HCl in the absence and presence of different concentrations of MnO nanoparticles.
The tabulated data indicate that increasing Mn₂O₃ concentration up to 20 ppm leads to **increase** of the charge transfer resistance $R_{ct}$ and **decrease** of $Q_{dl}$ values.

The metal protection at this concentration could be attributed to the adsorption of manganese ions on the mild steel surface.
3.3.2. Potentiodynamic Polarization curve measurement

Increasing concentration of the nanoparticles affect both:

- Anodic metal dissolution
- Cathodic hydrogen evolution processes.

Figure 3.2. Potentiodynamic polarization curves for steel in 0.5 M HCl in the absence and presence of different concentrations of Mn$_2$O$_3$ nanoparticles.
Table 3.2. Electrochemical polarization parameters for steel in 0.5 M HCl in the absence and presence of different concentrations of Mn$_2$O$_3$ nanoparticles

<table>
<thead>
<tr>
<th>Concentration of Mn$_2$O$_3$ (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$\beta_a$ (mV.dec$^{-1}$)</th>
<th>$\beta_c$ (mV.dec$^{-1}$)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>461</td>
<td>101</td>
<td>130</td>
<td>0.685</td>
</tr>
<tr>
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<td>434</td>
<td>98</td>
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<td>30</td>
<td>453</td>
<td>123</td>
<td>173</td>
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<td>80</td>
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<tr>
<td>60</td>
<td>441</td>
<td>112</td>
<td>205</td>
<td>2.961</td>
</tr>
</tbody>
</table>

$i_{corr}$ decreases with increasing Mn$_2$O$_3$ concentrations to 20 ppm showing the lowest $i_{corr}$. Slightly variation in values of the cathodic Tafel slope ($\beta_c$) in the region 0-20 ppm.

The corrosion is suggested to take place under adsorption/desorption mechanism.
Results obtained from potentiodynamic polarization curves measurements are in good agreement with those obtained from electrochemical impedance measurements. It could be concluded that the maximum inhibition is obtained in presence of 20 ppm Mn$_2$O$_3$. For this reason, 20 ppm was chosen for further study.
3.2. Effect of \( \text{Mn}_2\text{O}_3 \) nanoparticles synthesized at different pH.

3. 2.1. Open circuit potential measurements

The variation of the open circuit potential (OCP) with time is measured to define domains of corrosion.

Slight shift of the potential of steel to more noble direction is detected with decreasing pH.

Figure 3.3. Variation of the open circuit potential with time for steel in 0.5 M HCl solution in the absence and presence of 20 ppm \( \text{Mn}_2\text{O}_3 \) nanoparticles synthesized at different pH.
The shift of potential could be related to the larger particle size obtained at pH 10, that cover more active anodic sites controlling the anodic process.

<table>
<thead>
<tr>
<th>hkl</th>
<th>pH 10 Position (2Θ)</th>
<th>Particle Size (nm)</th>
<th>pH 11 Position (2Θ)</th>
<th>Particle Size (nm)</th>
<th>pH 12 Position (2Θ)</th>
<th>Particle Size (nm)</th>
<th>pH 13 Position (2Θ)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>211</td>
<td>23.36137</td>
<td>165</td>
<td>23.1528</td>
<td>112.8</td>
<td>23.15428</td>
<td>93.1</td>
<td>23.10891</td>
<td>74.3</td>
</tr>
<tr>
<td>222</td>
<td>33.16778</td>
<td>112</td>
<td>32.95805</td>
<td>99.7</td>
<td>32.9716</td>
<td>69.8</td>
<td>32.91796</td>
<td>67.7</td>
</tr>
<tr>
<td>400</td>
<td>38.46056</td>
<td>172</td>
<td>38.23637</td>
<td>138.1</td>
<td>38.25505</td>
<td>94.5</td>
<td>38.19352</td>
<td>67.1</td>
</tr>
<tr>
<td>322</td>
<td>45.36544</td>
<td>135.3</td>
<td>45.16352</td>
<td>111.1</td>
<td>45.18855</td>
<td>61.4</td>
<td>45.11715</td>
<td>53.8</td>
</tr>
<tr>
<td>431</td>
<td>49.48172</td>
<td>56</td>
<td>49.33871</td>
<td>94.9</td>
<td>49.36427</td>
<td>100.3</td>
<td>49.31172</td>
<td>71.8</td>
</tr>
<tr>
<td>440</td>
<td>55.36178</td>
<td>56.9</td>
<td>55.16523</td>
<td>86.5</td>
<td>55.19329</td>
<td>57.2</td>
<td>55.13766</td>
<td>65.6</td>
</tr>
<tr>
<td>622</td>
<td>65.93816</td>
<td>76.2</td>
<td>65.76458</td>
<td>104.6</td>
<td>65.78064</td>
<td>62.8</td>
<td>65.7395</td>
<td>61.1</td>
</tr>
</tbody>
</table>

**Average particle size (nm)**

- pH 10: 110.48
- pH 11: 106.81
- pH 12: 77.01
- pH 13: 65.91
3. 2.2. Electrochemical impedance spectroscopy result

The diameter of depressed semicircles increases with decreasing the pH.

Figure 3.4. Nyquist Impedance plots of steel in 0.5 M hydrochloric acid in the absence and presence of Mn$_2$O$_3$ nanoparticles synthesized at different pH.
The charge transfer resistance $R_{ct}$ and $Q_{dl}$ with decreasing pH.

This could be related to increase of particle size with decreasing pH.

The inhibition takes place through adsorption mechanism.
3.2.3. Potentiodynamic polarization measurements

Figure 3.5. Potentiodynamic polarization curves for steel in 0.5 M HCl in the absence and presence of 20 ppm of Mn₂O₃ nanoparticles at different pH.
The nanoparticles synthesized at pH = 10, with the highest nanoparticles size, have the lowest $i_{corr}$ and highest $\%\eta$. 

Table 3.5. Electrochemical polarization parameters and $\%\eta$ for steel in 0.5M HCl in the absence and presence of 20 ppm Mn$_2$O$_3$ nanoparticles synthesized at different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>-E$_{corr}$ (mV)</th>
<th>$\beta_a$ (mV.dec$^{-1}$)</th>
<th>$\beta_c$ (mV.dec$^{-1}$)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
<th>$%\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M HCl</td>
<td>461</td>
<td>101</td>
<td>130</td>
<td>0.685</td>
<td>-</td>
</tr>
<tr>
<td>pH 10</td>
<td>442</td>
<td>82</td>
<td>110</td>
<td>0.319</td>
<td>53.34</td>
</tr>
<tr>
<td>pH 11</td>
<td>441</td>
<td>85</td>
<td>112</td>
<td>0.432</td>
<td>36.93</td>
</tr>
<tr>
<td>pH 12</td>
<td>444</td>
<td>80</td>
<td>113</td>
<td>0.448</td>
<td>34.59</td>
</tr>
<tr>
<td>pH 13</td>
<td>438</td>
<td>86</td>
<td>120</td>
<td>0.527</td>
<td>23.06</td>
</tr>
</tbody>
</table>
Both techniques confirm

• The role of 20 ppm of Mn$_2$O$_3$ nanoparticles synthesized at pH 10, in improving the electrochemical corrosion behaviour of mild steel in 0.5 M HCl.

• The efficiency was found to increase with decreasing pH.
3.3. Effect of Mn$_2$O$_3$ nanoparticles synthesized at pH 10 in 0.5 M H$_2$SO$_4$ and 0.5 M H$_3$PO$_4$.

The impedance has been changed after the addition of Mn$_2$O$_3$ nanoparticles to the 0.5 M H$_2$SO$_4$ and 0.5 M H$_3$PO$_4$ solution.

Figure 3.6. Nyquist impedance plots of mild steel in 0.5 M H$_2$SO$_4$ and 0.5 M H$_3$PO$_4$ in the absence and presence of 20 ppm Mn$_2$O$_3$ nanoparticles synthesized at pH 10.
Similar trend of inhibition efficiency to that obtained from impedance measurements.

The inhibition efficiency of nanoparticles in HCl should be the highest and that in H$_2$SO$_4$ is the lowest.
The inhibition efficiency increases in the order HCl > H₃PO₄ > H₂SO₄.
In acidic solution, Mn$_2$O$_3$ nanoparticles are reduced to Mn$^{2+}$ according to the following equation:

\[
\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + \text{e}^- \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}
\]

The metal protection could be attributed to the adsorption of manganese ions on the mild steel surface. The adsorbed cations act as a protective layer, reducing the interaction between the aggressive ions and the steel surface.
Conclusions

- In this study, the effect of $\text{Mn}_2\text{O}_3$ nanoparticles addition on mechanical and corrosion behavior of Sm-123 superconducting phase in 0.5 M HCl was investigated.

- $\text{Mn}_2\text{O}_3$ nanoparticles were synthesized at different pH values ranging from 10 to 13 by co-precipitation technique.

- Superconducting samples of type $(\text{Mn}_2\text{O}_3)_x \text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $0.00 \leq x \leq 0.08$ wt. % were prepared by the conventional solid-state reaction technique.

- $\text{Mn}_2\text{O}_3$ nanoparticles showed a dependence on pH and particle size.

- The analysis of the mechanical properties of $(\text{Mn}_2\text{O}_3)_x \text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ showed that the microhardness parameters increase with increasing nano- addition from 0.00 to 0.02 wt%. 
Conclusions

• The electrochemical behavior of Sm-123 phase superconductor can be improved by the addition of Mn$_2$O$_3$ nanoparticles in 0.5 M HCl.

• This nano-addition can lead to the decreasing of the pores diameter and filling up of voids and cracks and hence, increasing in grain connectivity and reducing the penetration of ionic species into the superconductor material.

• Mn$_2$O$_3$ nanoparticle doped Sm-123 phase superconductor can act as a mixed type inhibitor and can be a promoted material for applications in many fields.
QUESTIONS?

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Thank you