prh anp

Encontro Nacional do Programa de Formação de Recursos Humanos da ANP - 2026

Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi_2O_2CO_3$ nanosheets

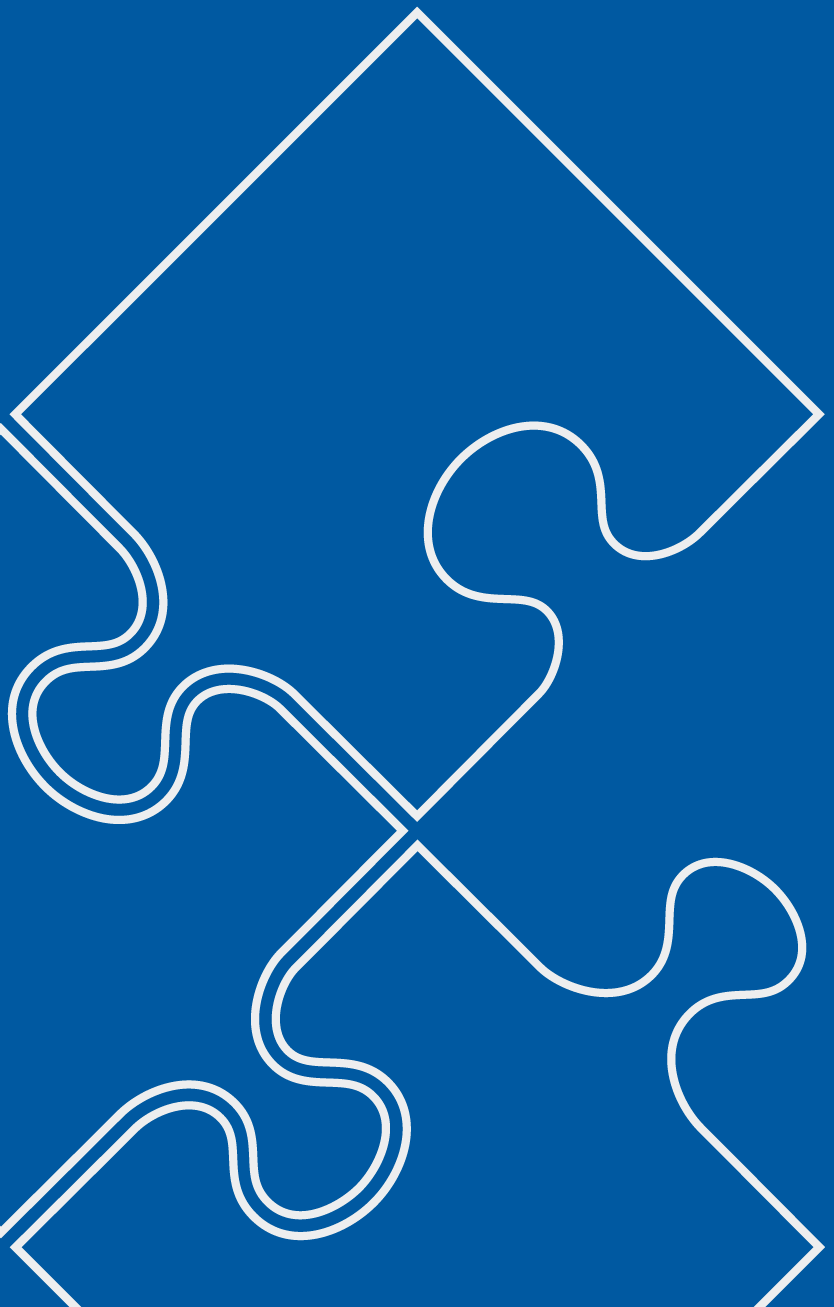
Cleiton Policarpo; Ernesto; Caue Ribeiro.

PRH 06 – ANP/UFSCar

Bolsa PRH: Doutorado

Universidade Federal de São Carlos - UFSCar

anp | Gestão: FAPESP



#1

MOTIVAÇÃO

Alternativas para a redução de CO_2

EMISSÕES DE GASES DO EFEITO ESTUFA

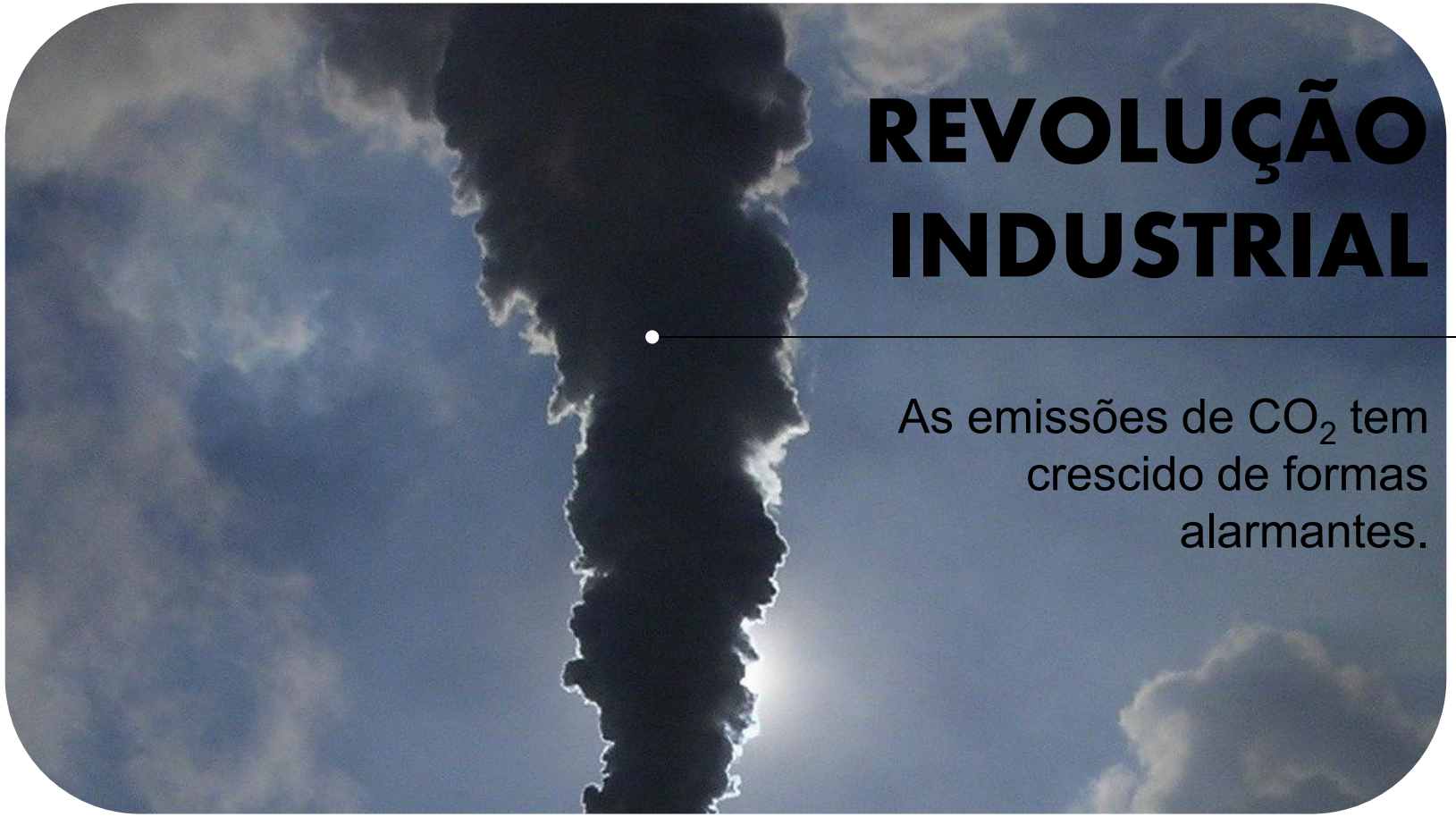


Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi2O_2CO_3$ nanosheets

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EMISSÕES DE GASES DO EFEITO ESTUFA



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ATIVIDADE ANTROPOGÊNICAS

A queima de combustíveis fosseis é a principal responsável pelos gases do efeito estufa.



LIU, **Solar RRL**, v. 5, 2021.

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CRESCENTE PREOCUPAÇÃO

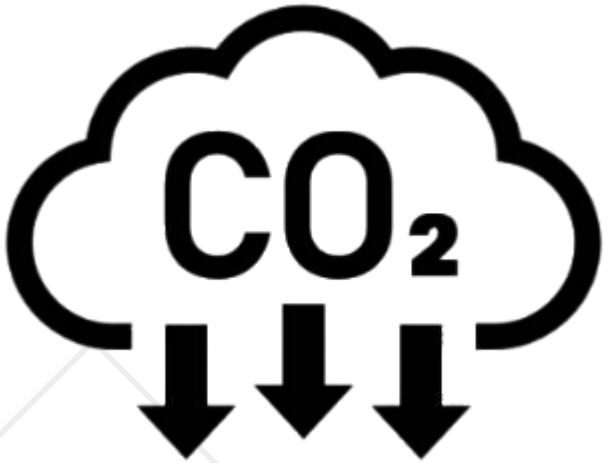
Com as mudanças climáticas surge o protocolo de Kyoto e o acordo de Paris.

REDUÇÃO ELETROQUÍMICA DE CO_2

Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi2O_2CO_3$ nanosheets

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A redução eletroquímica de CO_2 tem se mostrado uma boa alternativa para a problemática do CO_2

01 | Controle de seletividade pelo potencial

02 | Reciclagem de eletrólito

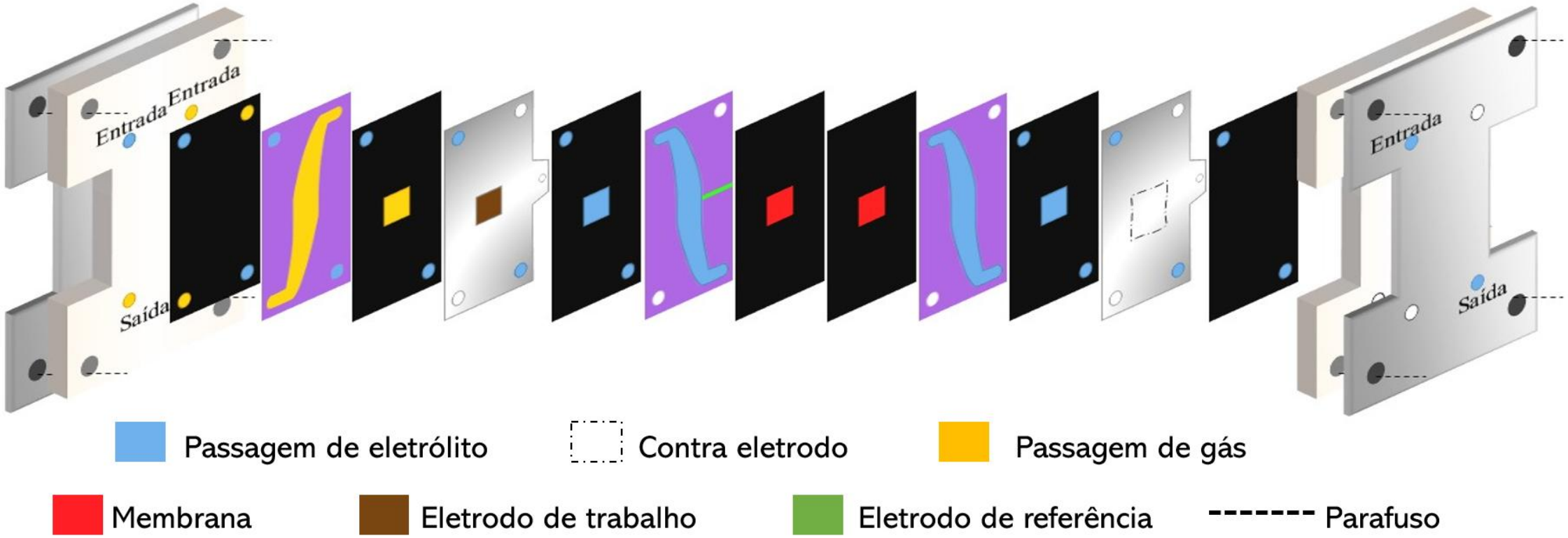
03 | Energia advinda de fontes renováveis

04 | Sistemas compactos e modulares

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Célula Eletroquímica em Fluxo



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Redução eletroquímica de CO_2 e seus correspondentes potenciais de redução E° (V vs EPH em pH 7.0).

Produtos	Equação	E° (V)
Ânion radical carbonato	$CO_2 + e^- \rightarrow CO_2^-$	-1,85
Ácido fórmico	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0,61
Monóxido de carbono	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0,53
Formaldeído	$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0,48
Metanol	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0,38
Metano	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0,24
Etileno	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	-0,34
Etanol	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 4H_2O$	-0,33
Etano	$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	-0,27
Propanol	$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 5H_2O$	-0,32

Principais vantagens do HCOOH

Facilidade em armazenar e transportar

Uso em células a combustível

Aplicação direta ou na fabricação de outros produtos

Baixa toxicidade

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Objetivos de Desenvolvimento Sustentável



Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi2O_2CO_3$ nanosheets

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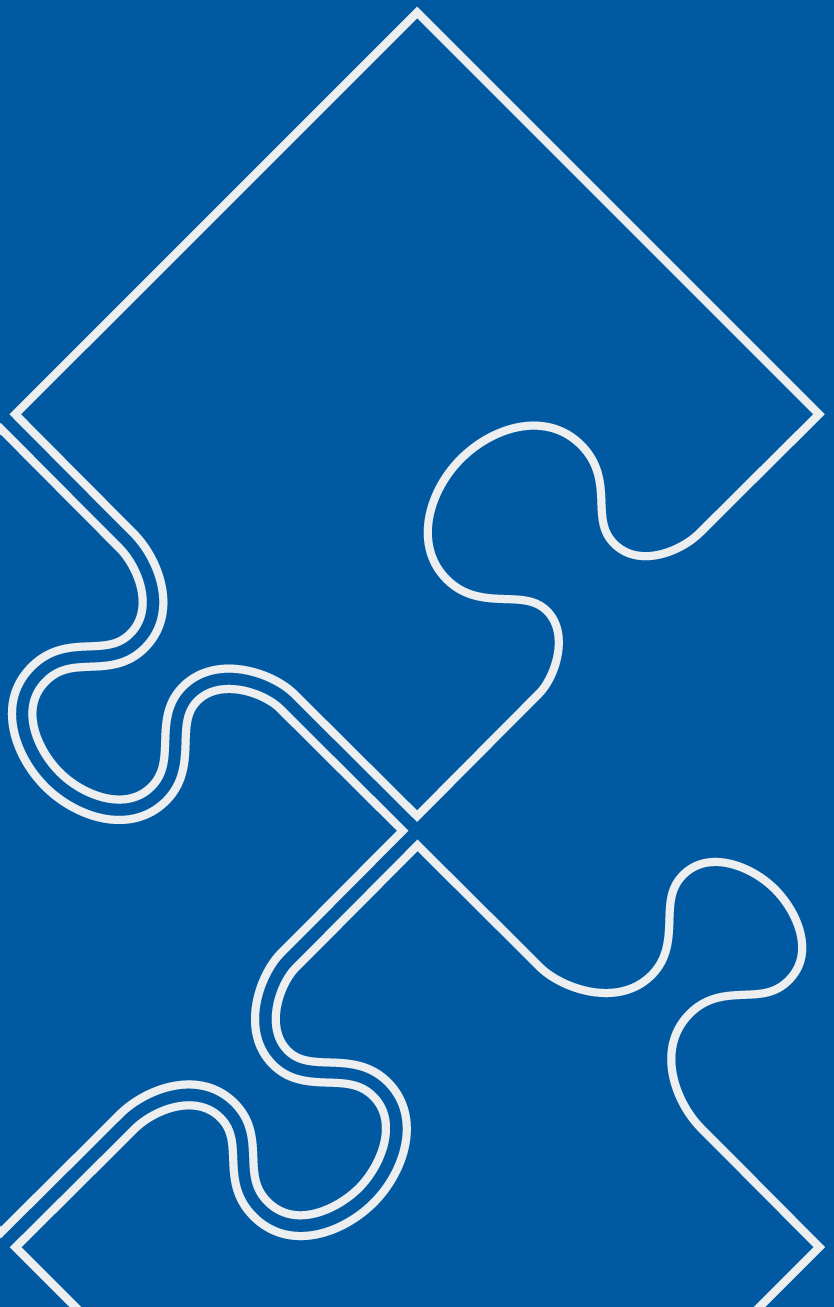
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#2

MATERIAIS E METODOS

Confecção dos eletrodos de difusão gasosa.

2 - METODOLOGIA

2.1 Síntese de amostras de $Bi_2O_2CO_3$ e Bi_2O_3

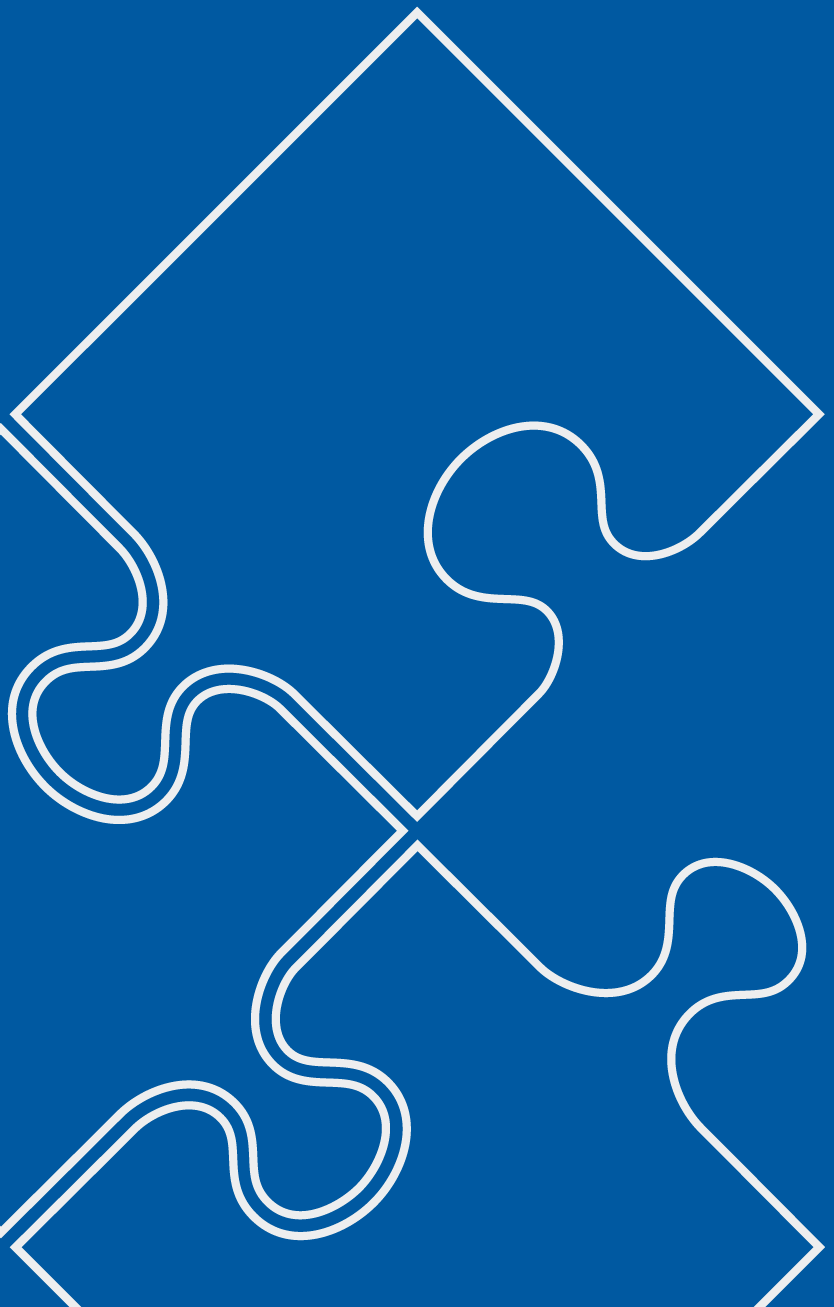


2.2 Preparação de eletrodos de difusão de gás



Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi2O_2CO_3$ nanosheets

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#3

RESULTADOS E DISCUSSÕES

Caracterização físico-química e desempenho dos catalisadores

3 – Caracterização Físico-Química

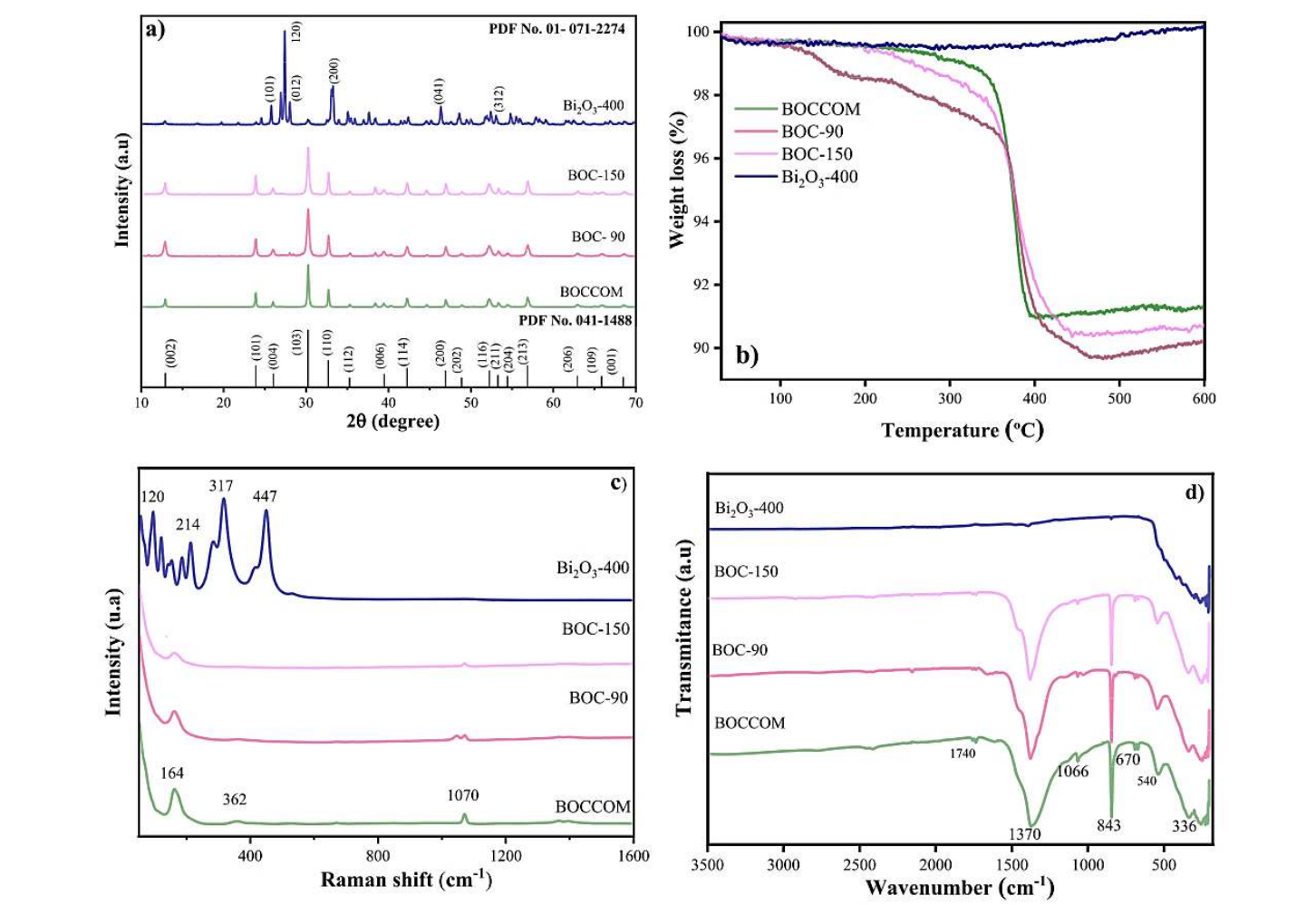


Fig. 1. a) XRD patterns b)TGA analysis **c)** Raman scattering spectra and **d)** ATR-FTIR spectra of the BOCCOM, BOC-90, BOC-150, and Bi_2O_3–400 samples.

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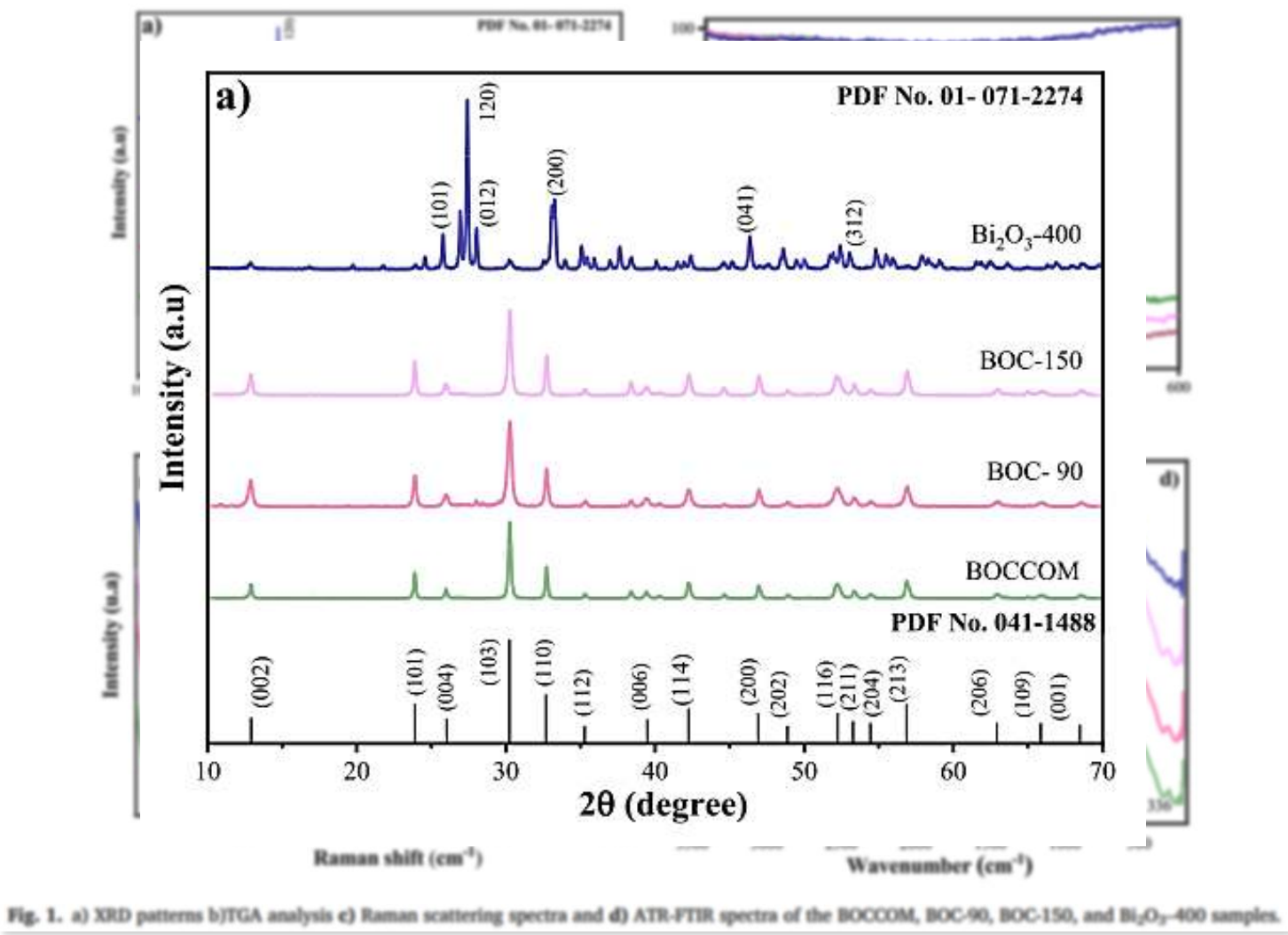


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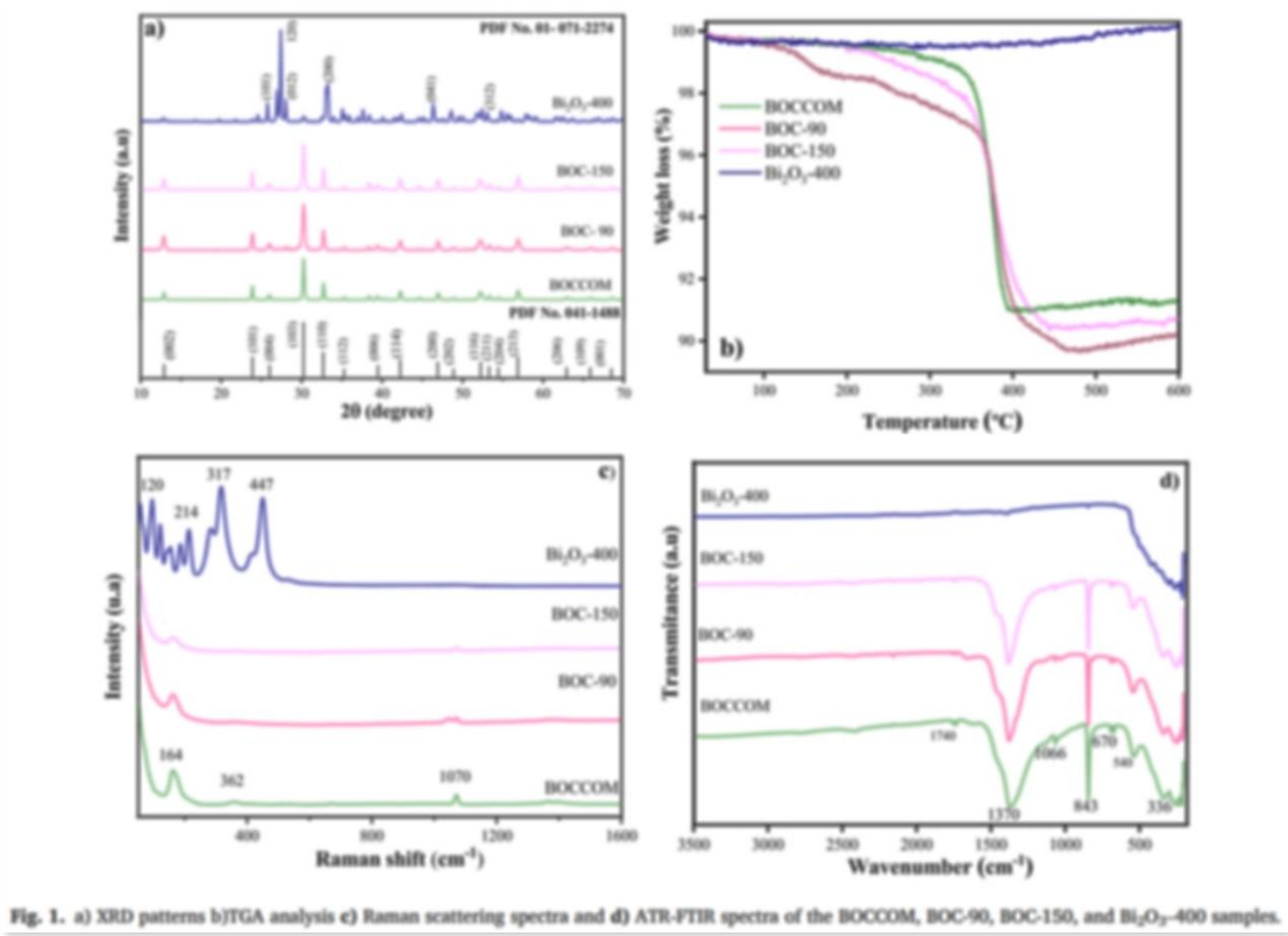


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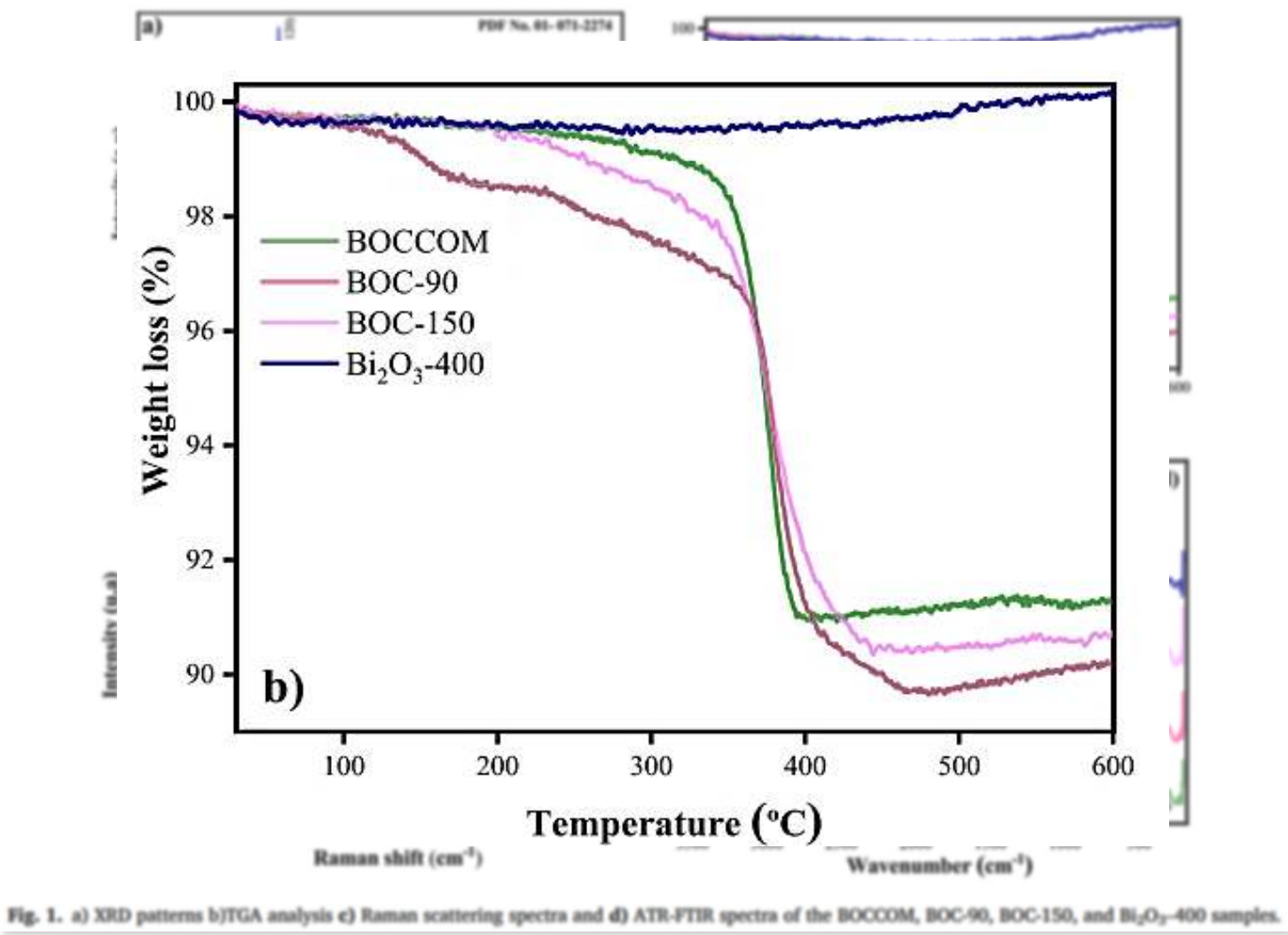


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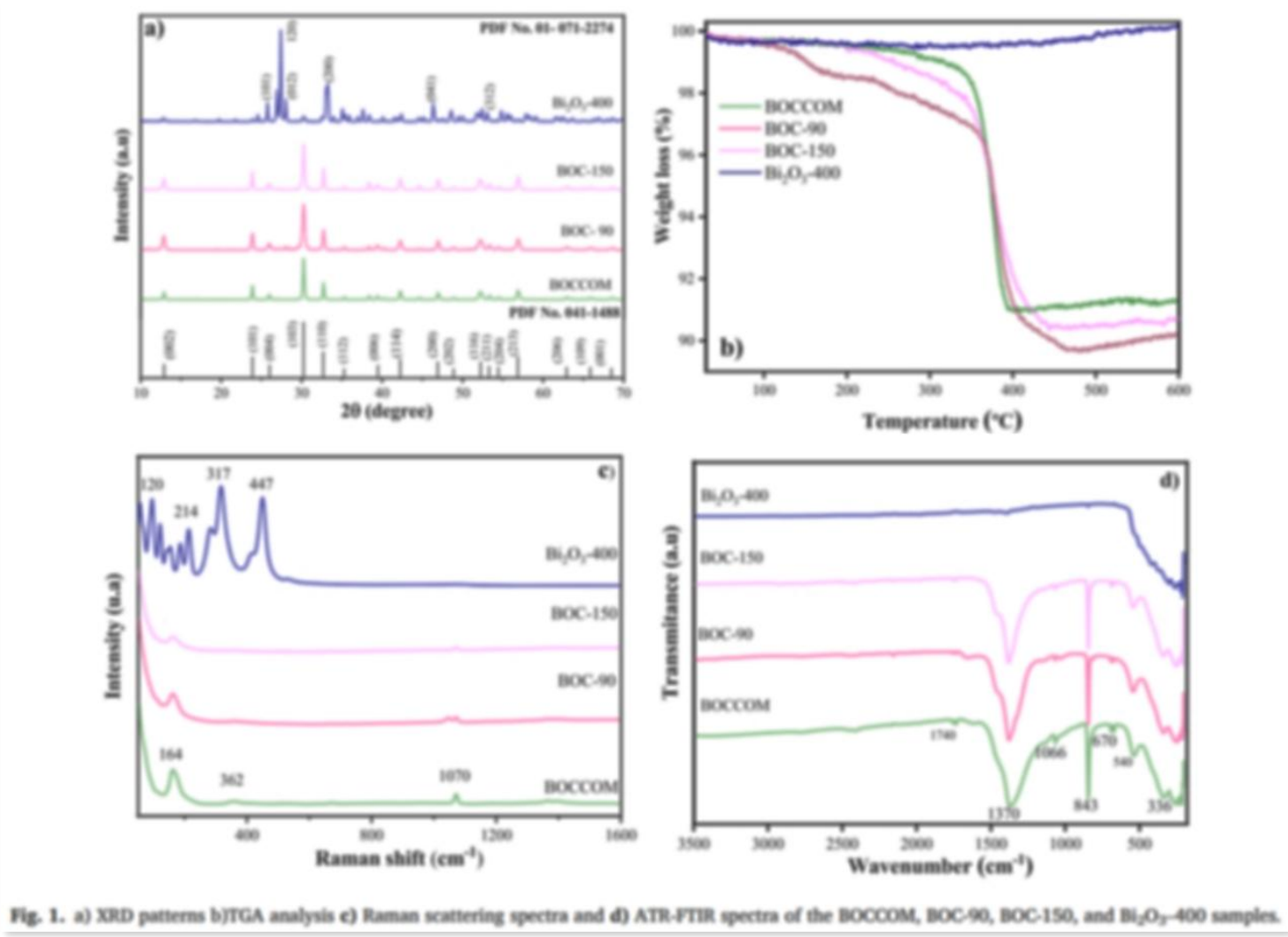


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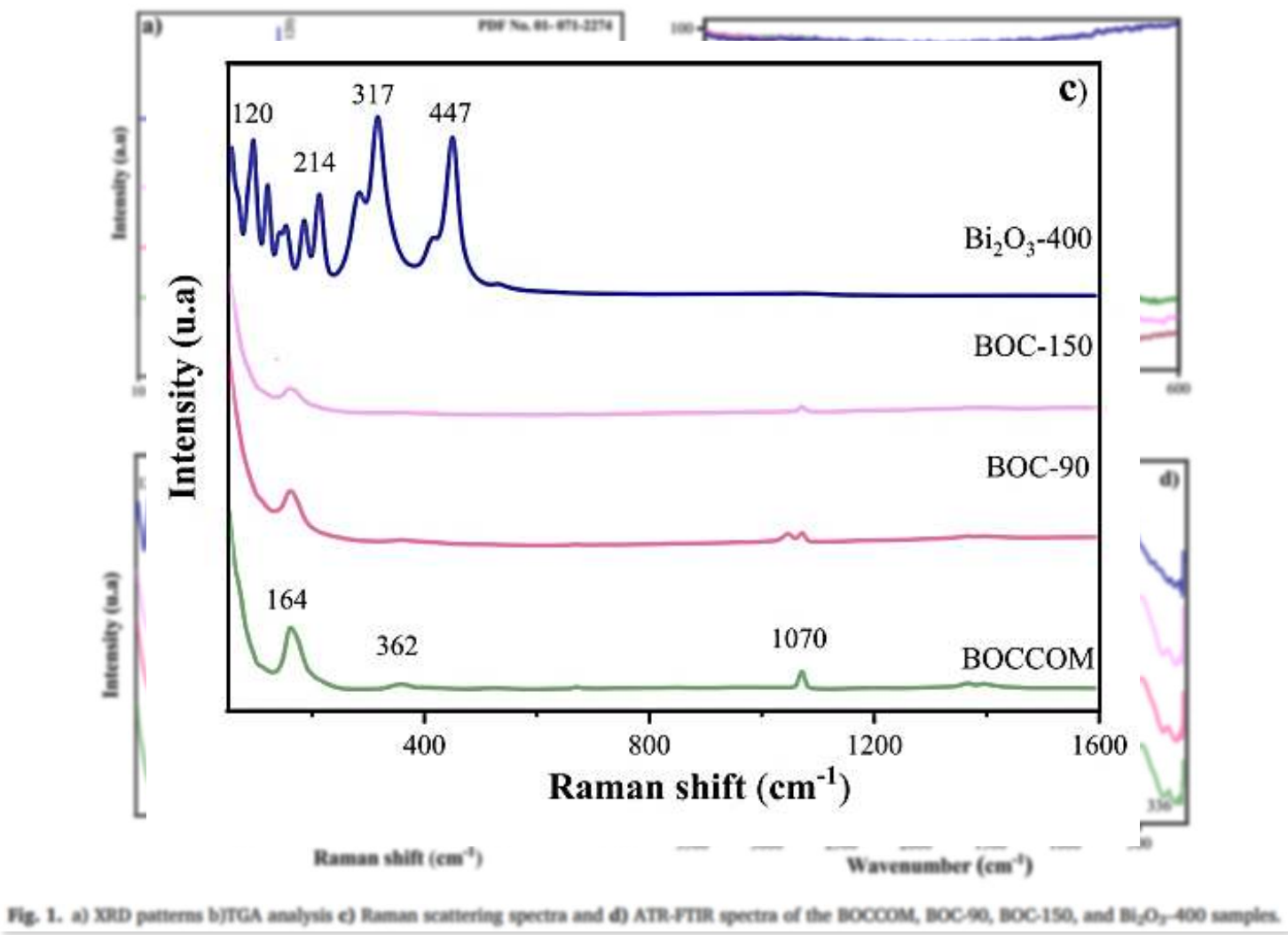


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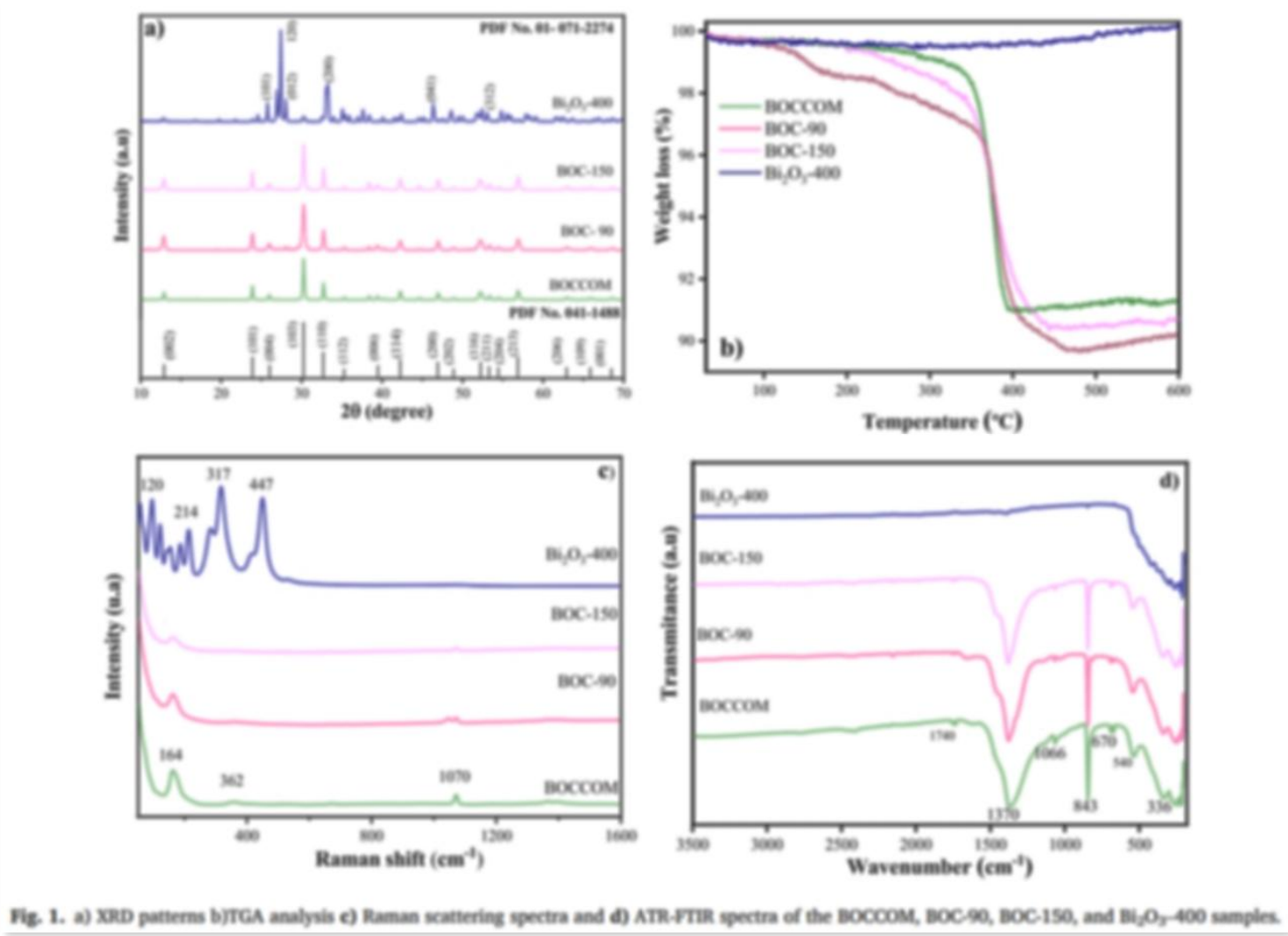


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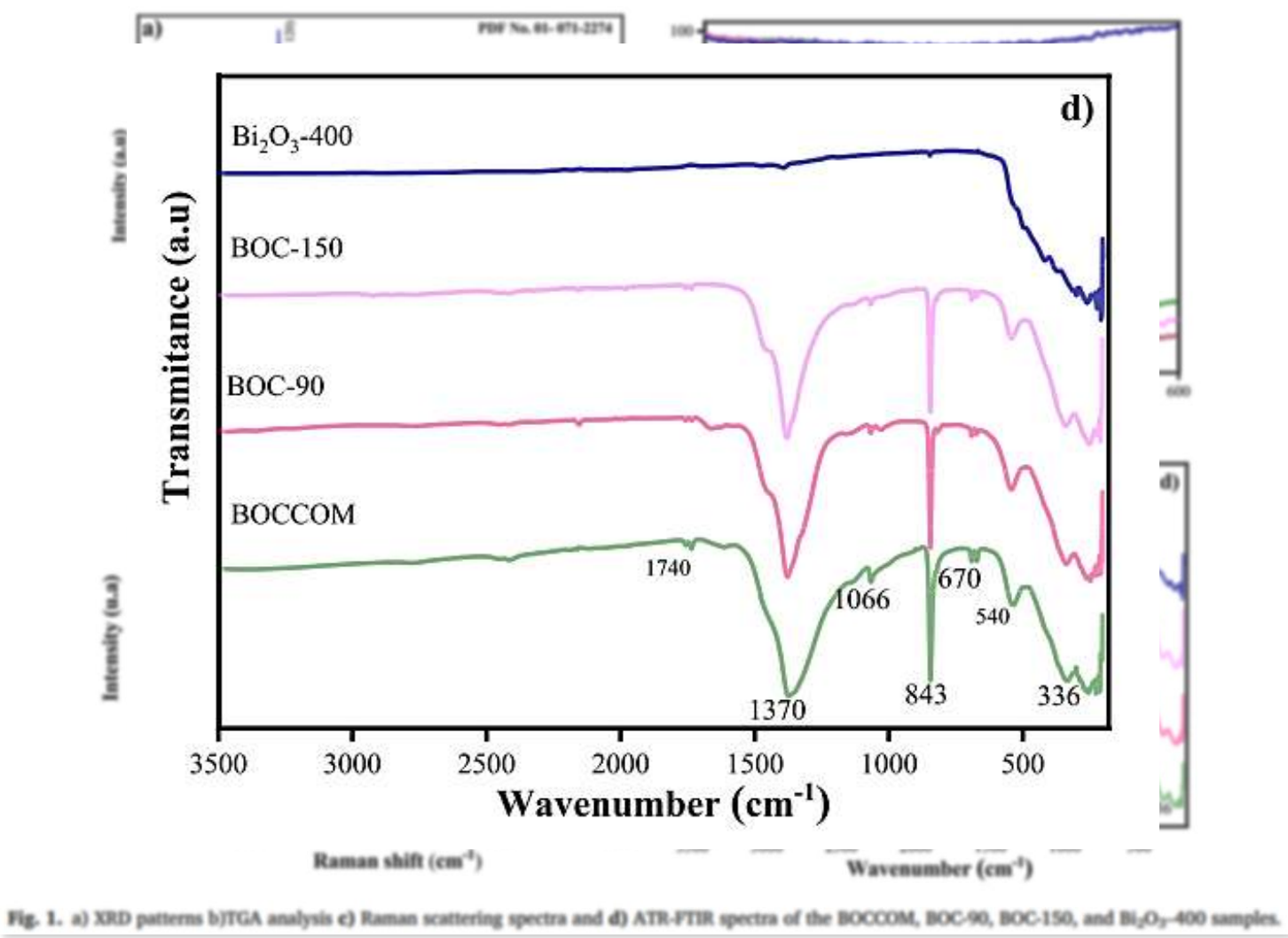


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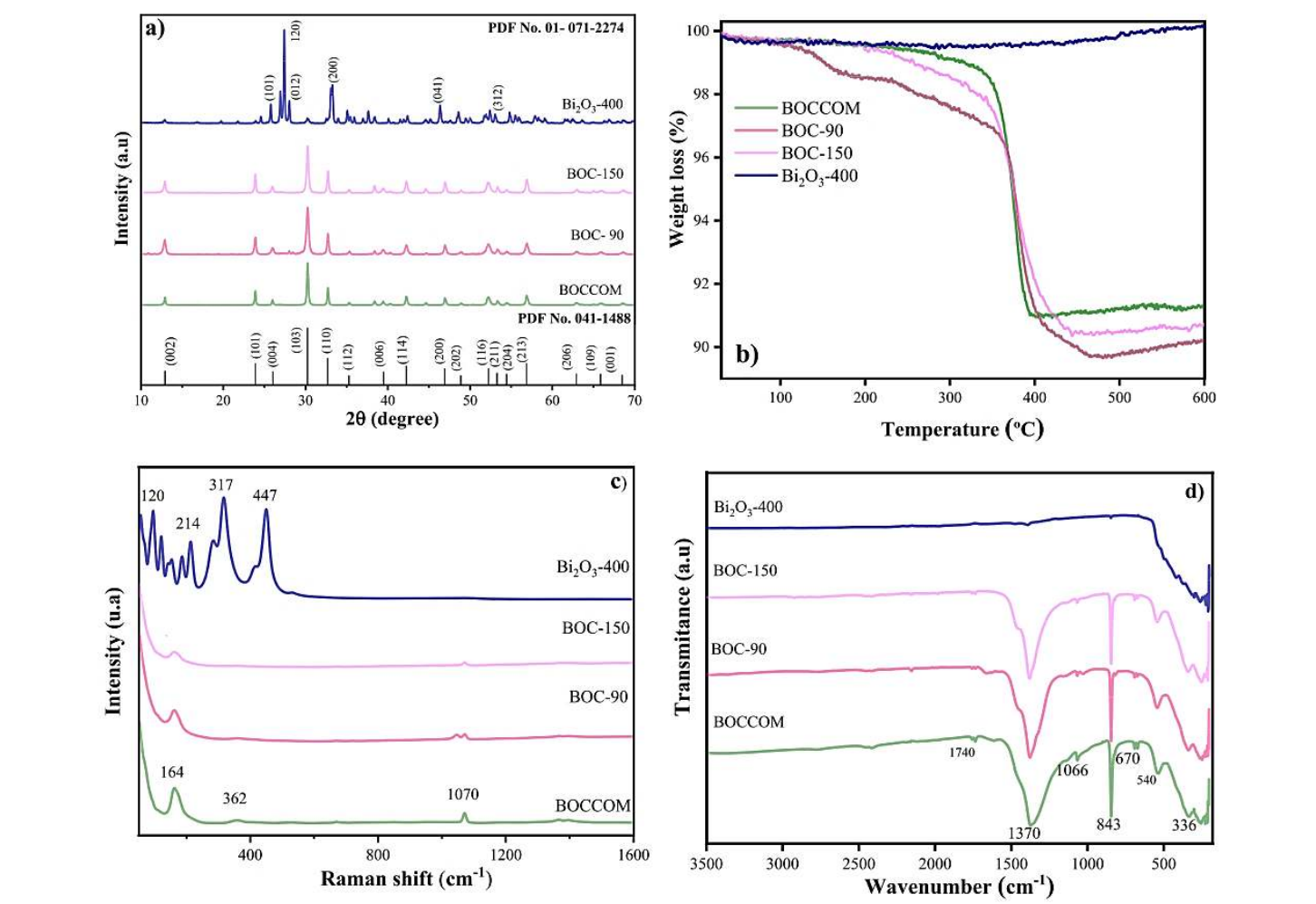


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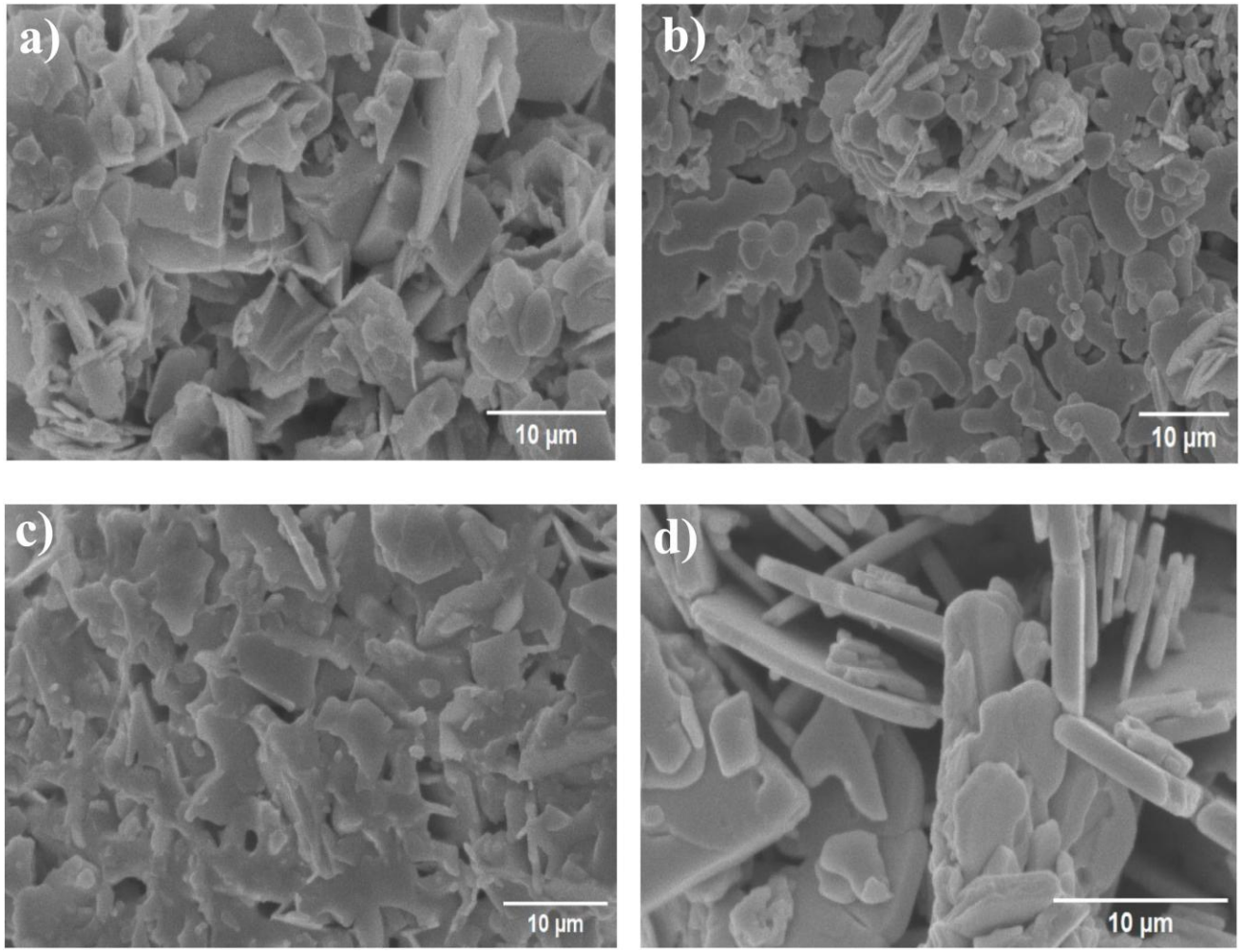


Fig. 2. SEM images of the synthesized samples **(a)** BOC-90, **(b)** BOC-150, **(c)** Bi_2O_3–400, and **(d)** BOCCOM.

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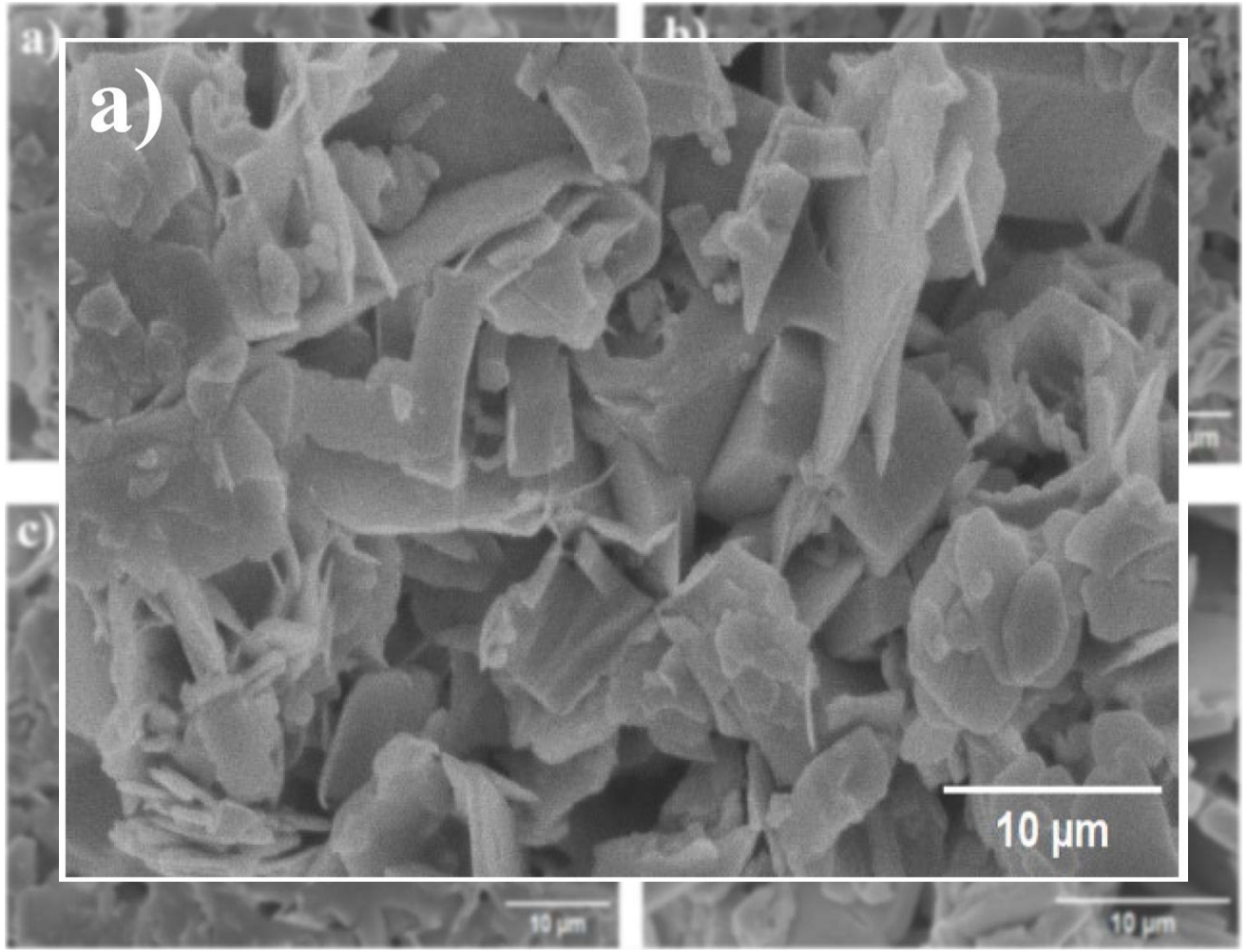


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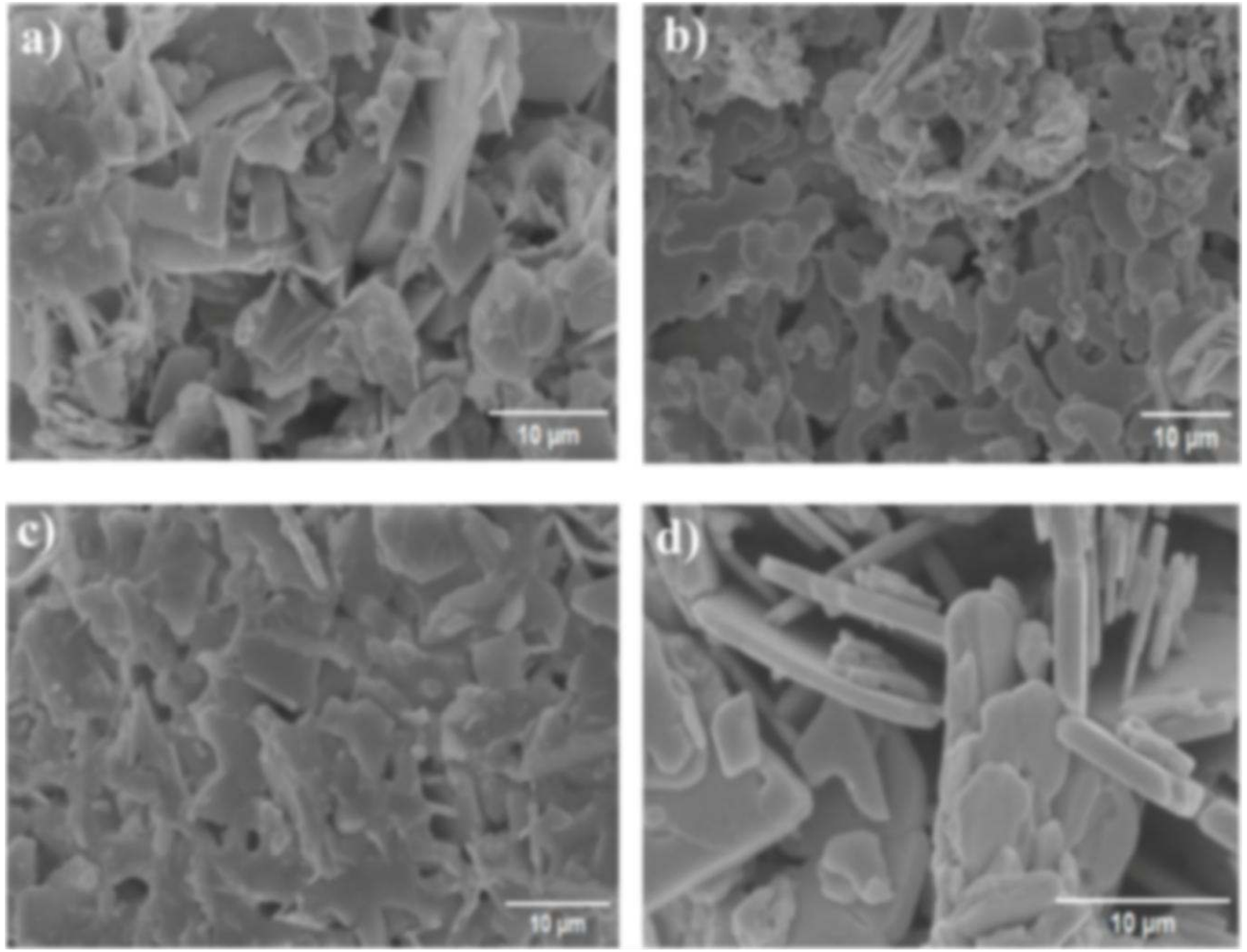


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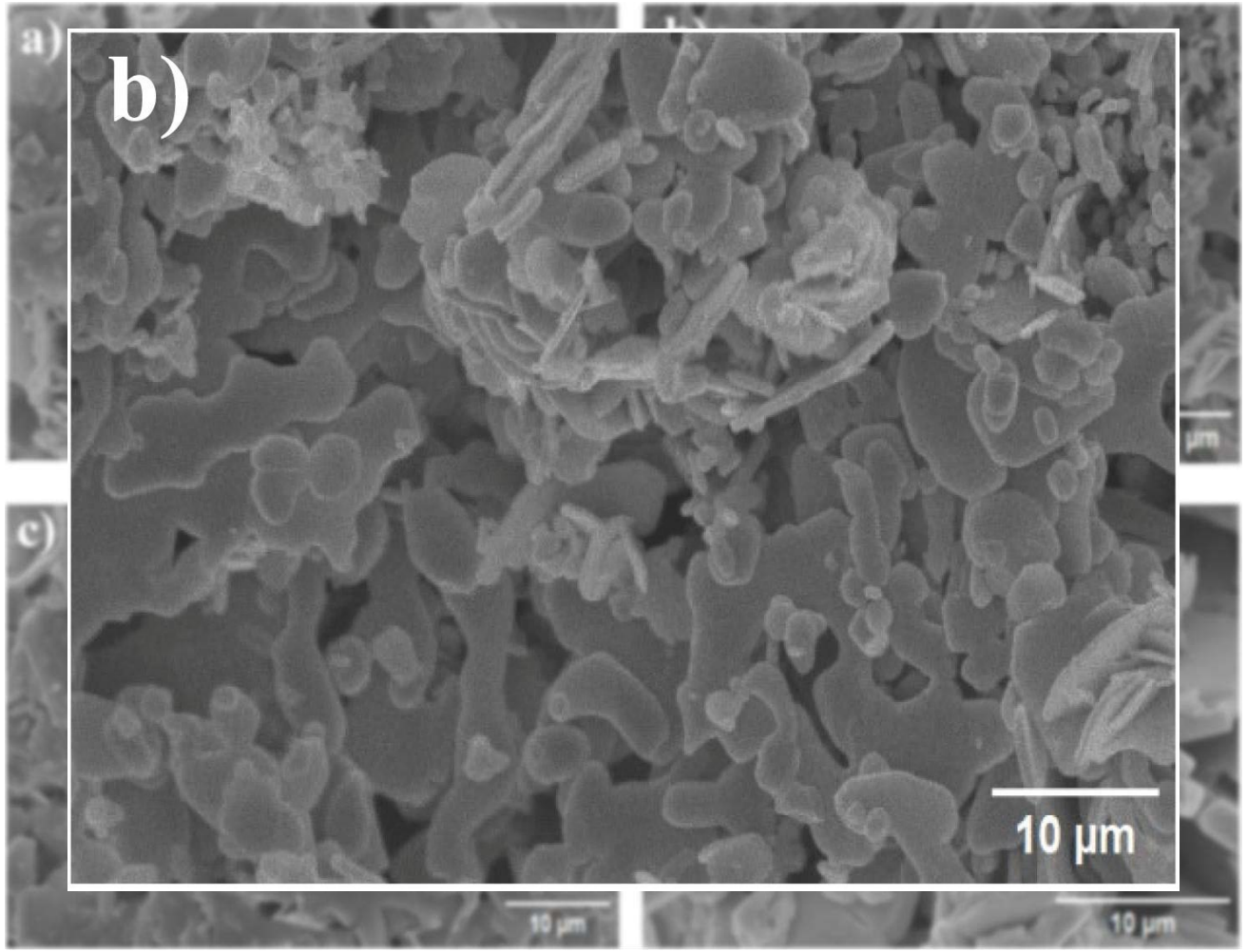


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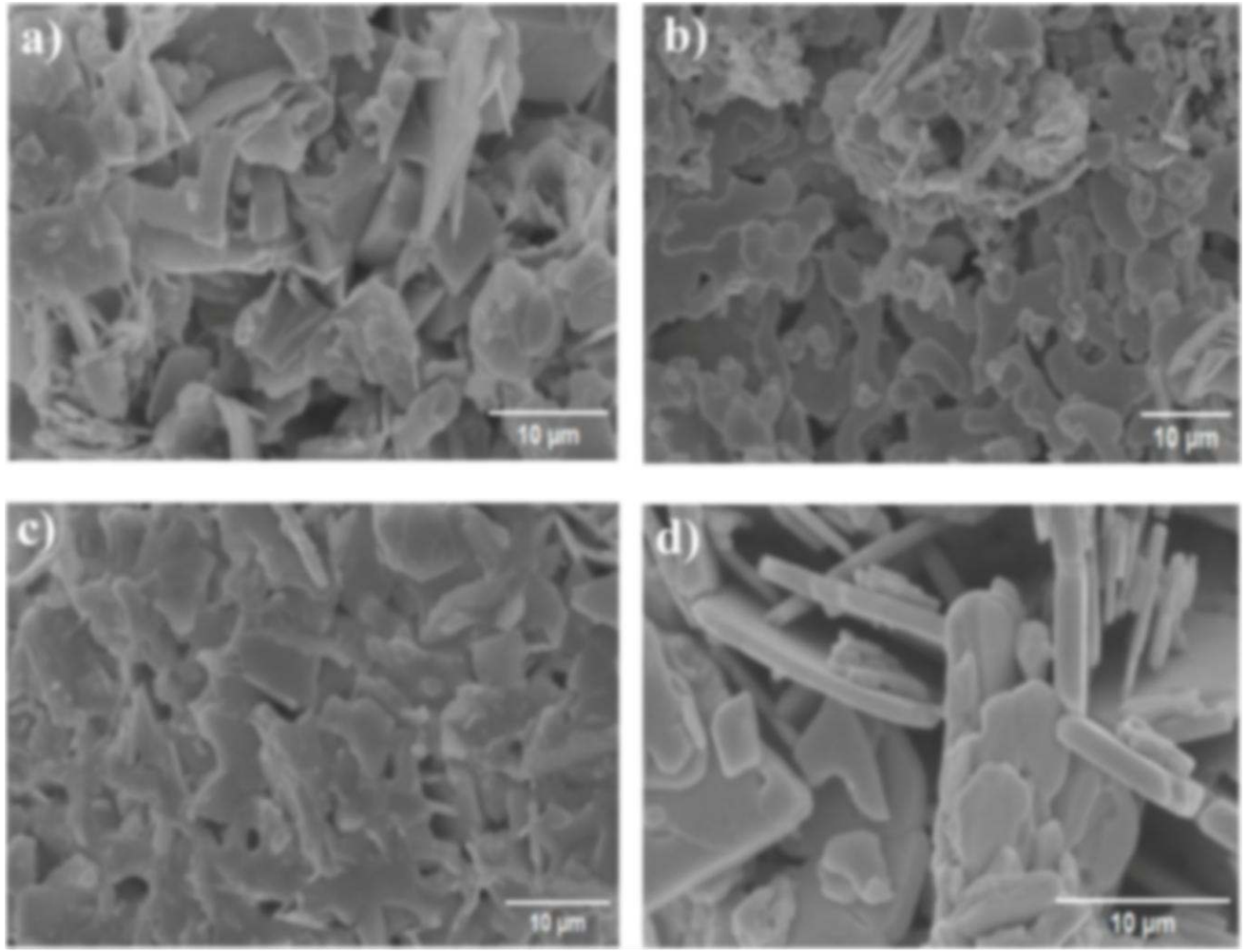


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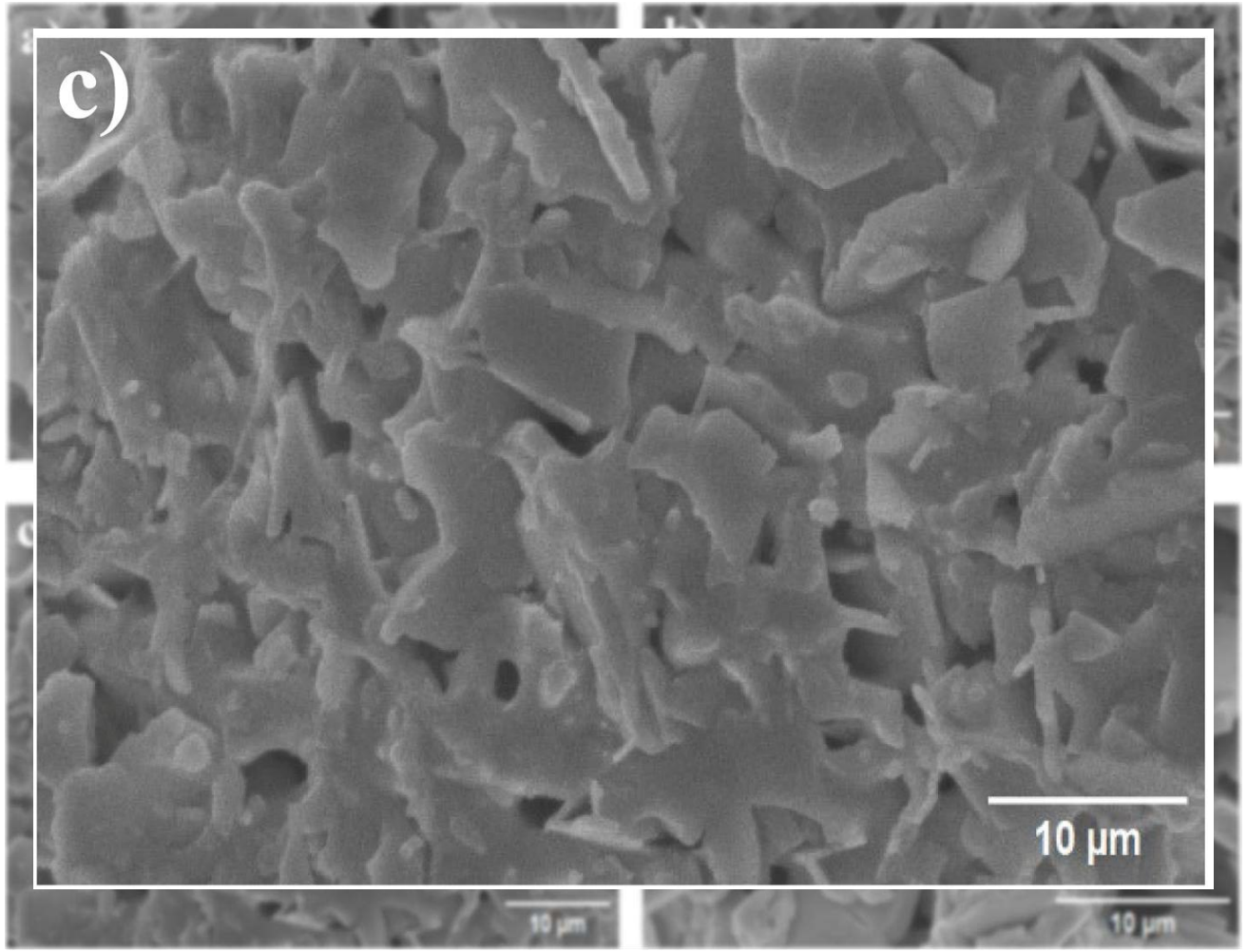


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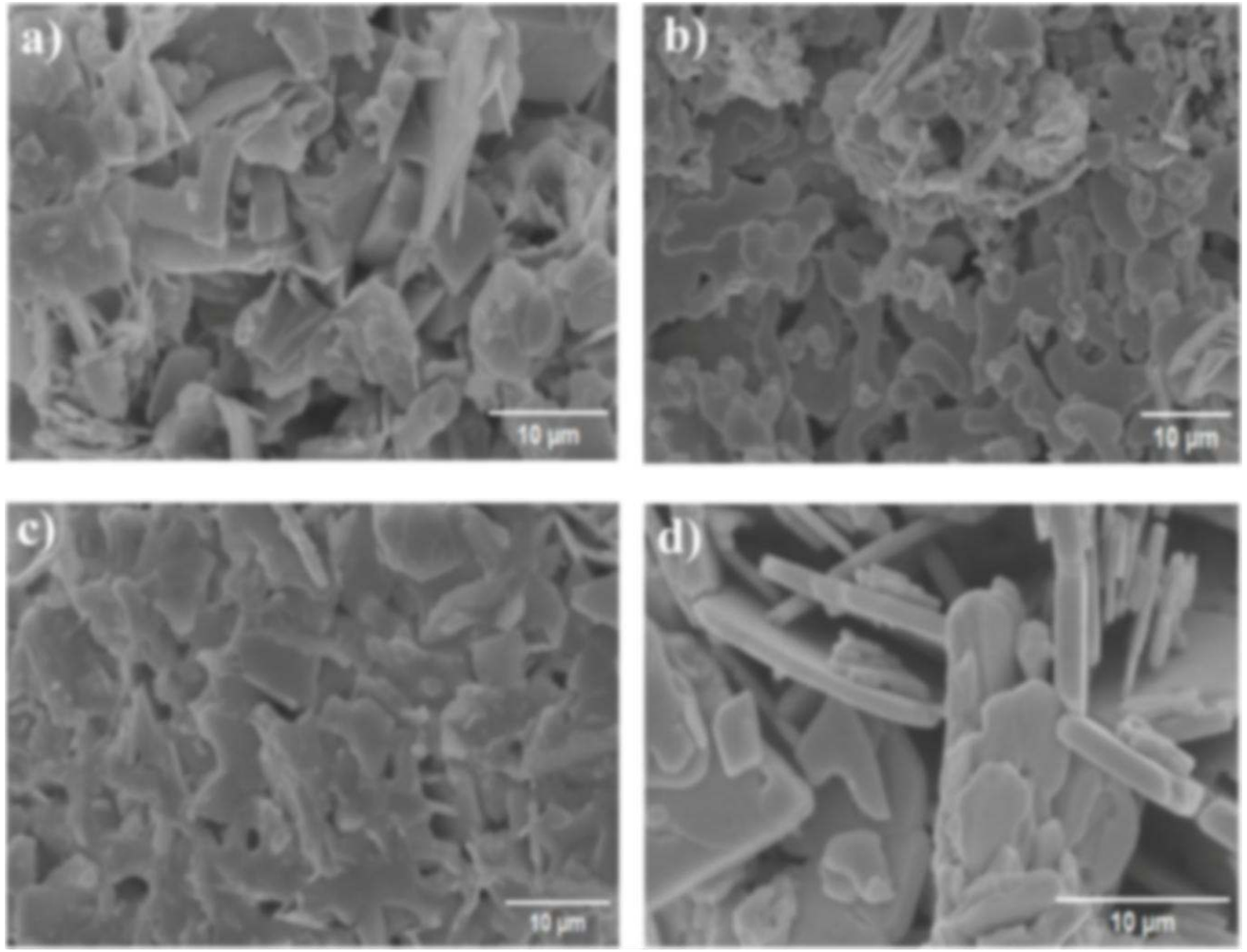


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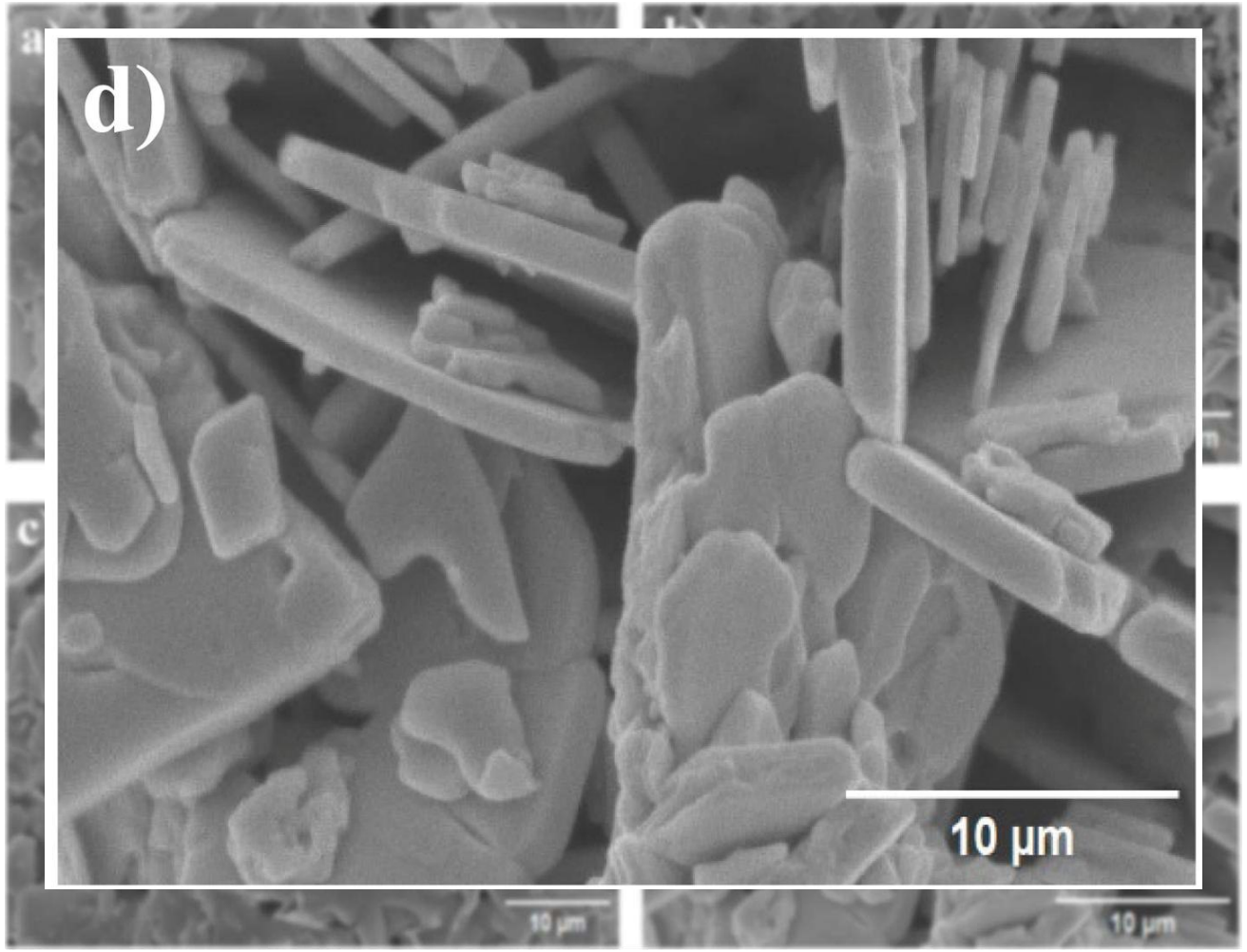


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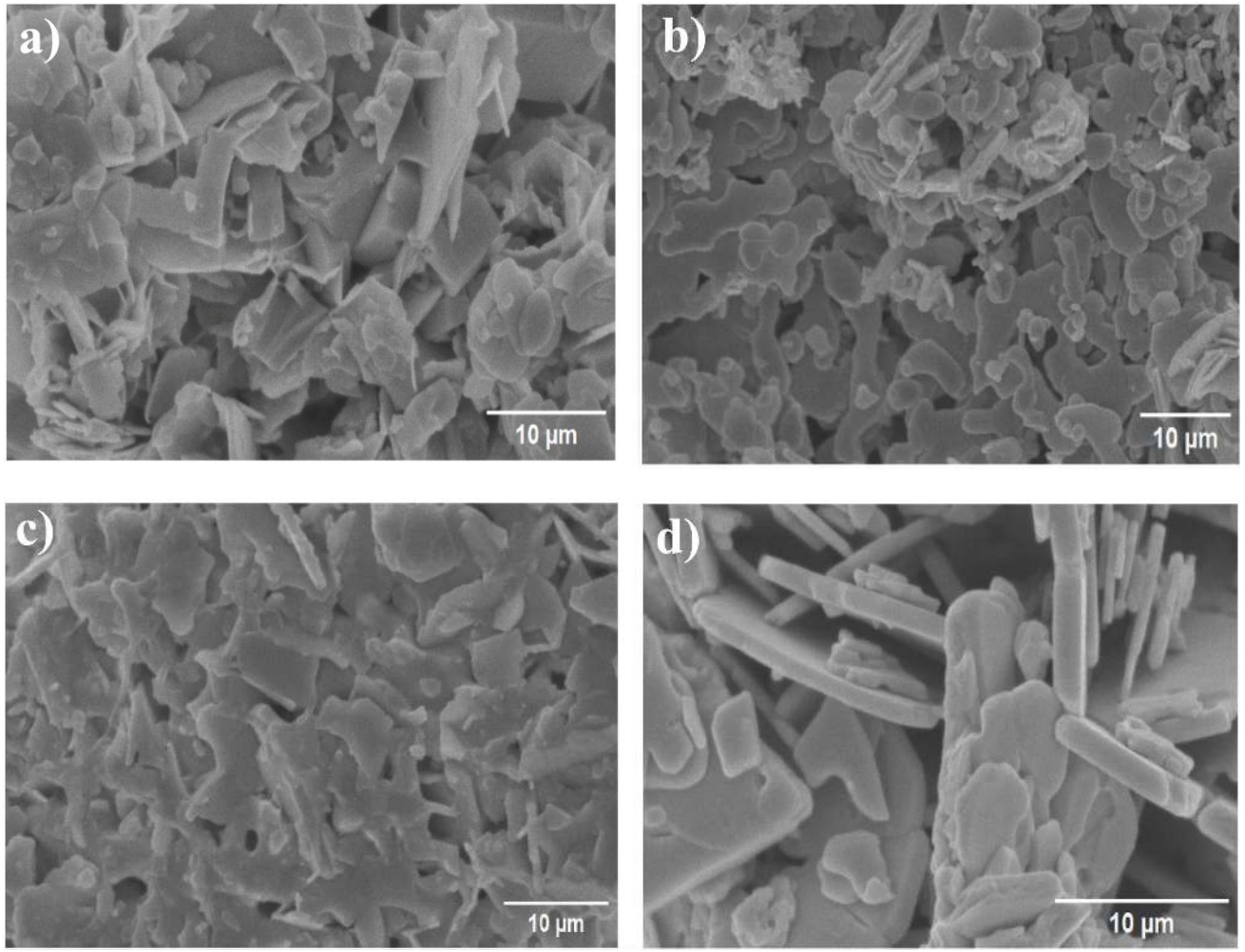
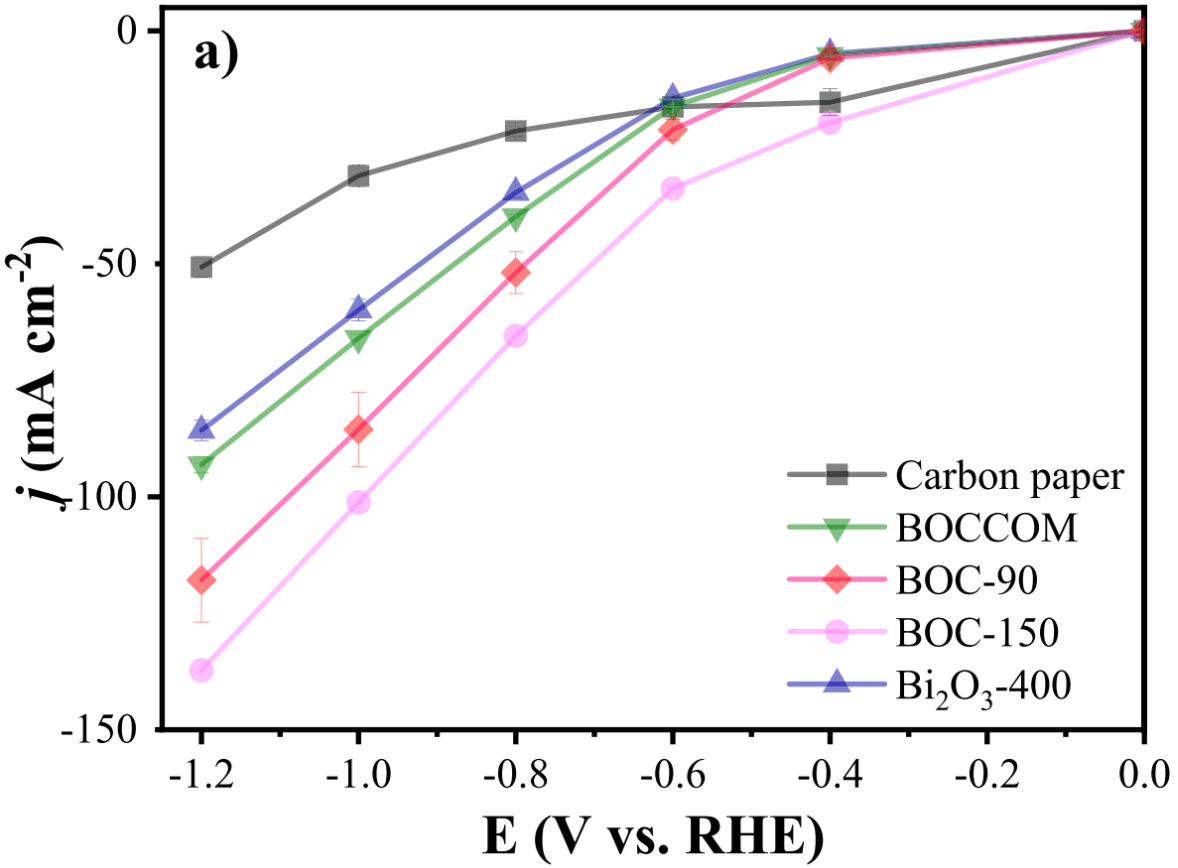


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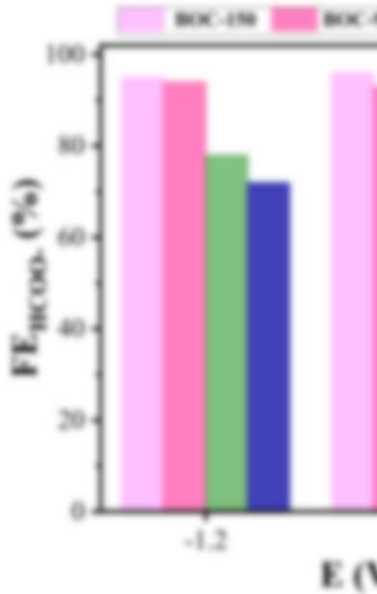


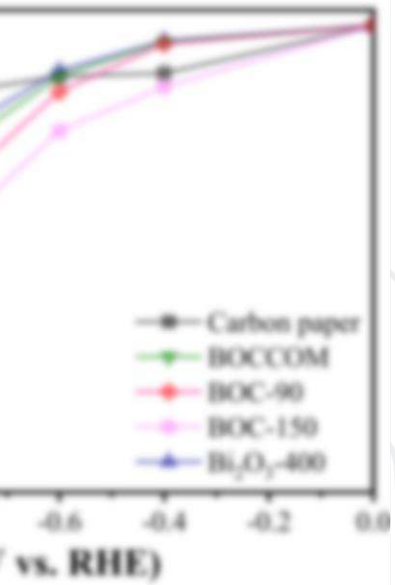
Fig. 3. **(a)** LSV curves for carbon paper and BOC samples in 0.5 M KOH electrolyte in a electrochemical flow cell, applying potential range of −0.4 to −1.2 vs. RHE. **(b)** FE_{HCOO^-} obtained at corresponding applied potential (−0.8 to −1.2 V) during 30 min. Carbon paper is not included in panel (b) because no HCOO- production was detected.

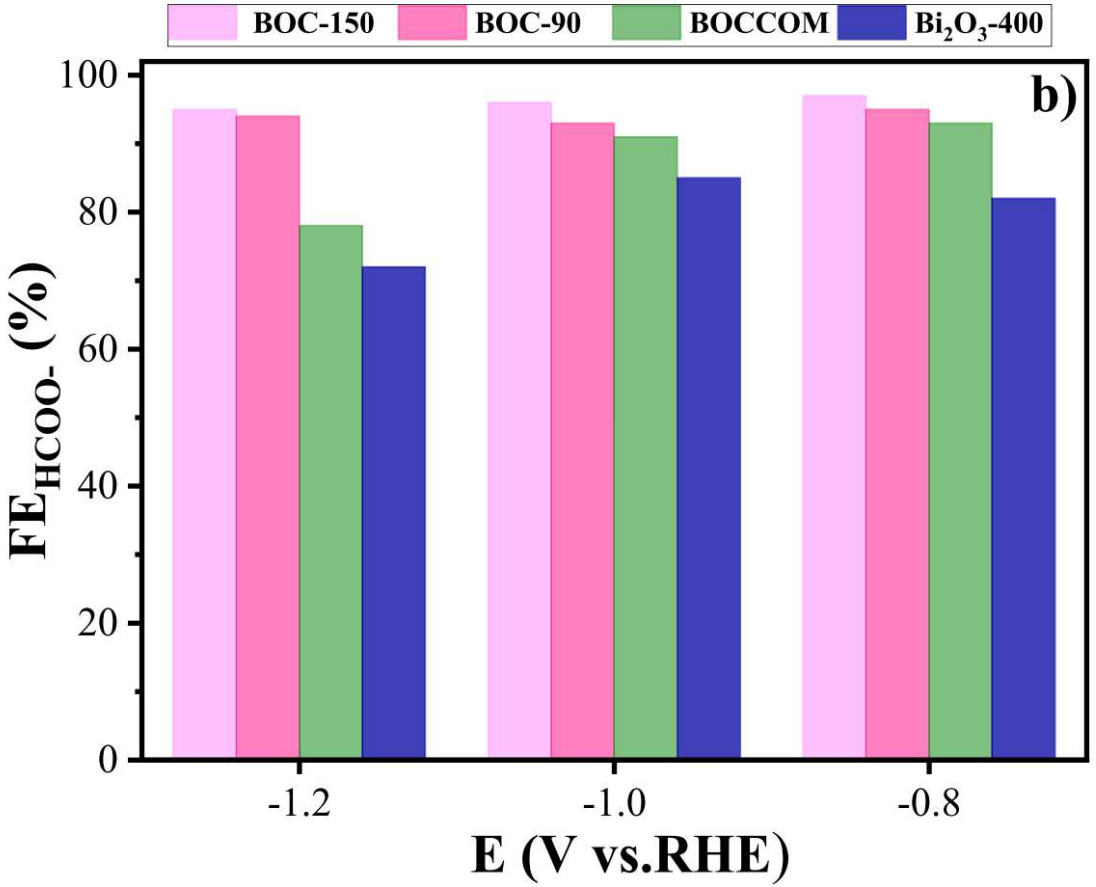
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3 – Caracterização Físico-Química





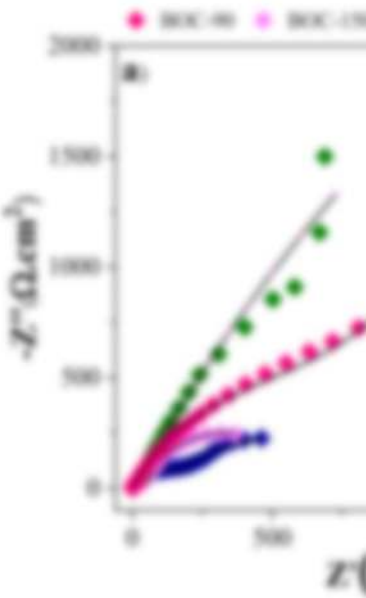


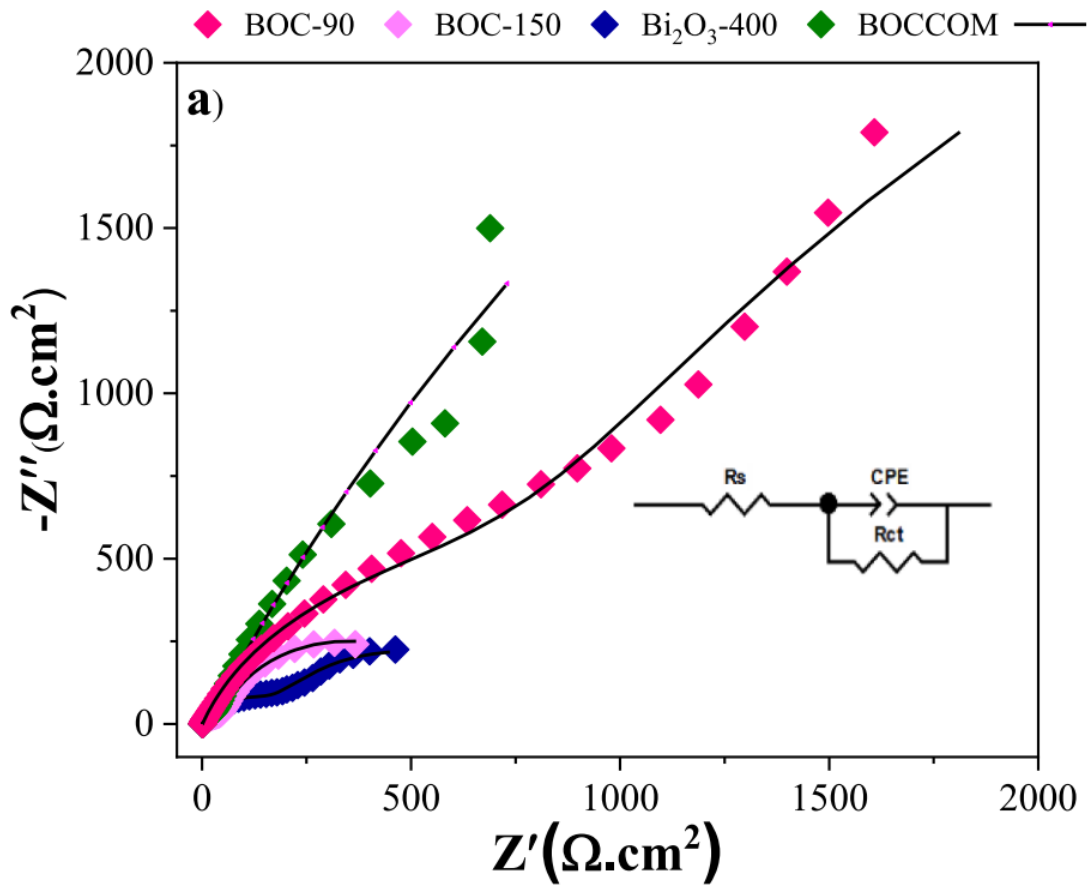
Fig. 3. **(a)** LSV curves for carbon paper and BOC samples in 0.5 M KOH electrolyte in a electrochemical flow cell, applying potential range of −0.4 to −1.2 vs. RHE. **(b)** FE_{HCOO-} obtained at corresponding applied potential (−0.8 to −1.2 V) during 30 min. Carbon paper is not included in panel (b) because no HCOO- production was detected.

Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi2O_2CO_3$ nanosheets

Cleiton Policarpo – Bolsa PRH: Doutorado
PRH 06 – ANP/UFSCar

3 – Caracterização Físico-Químico





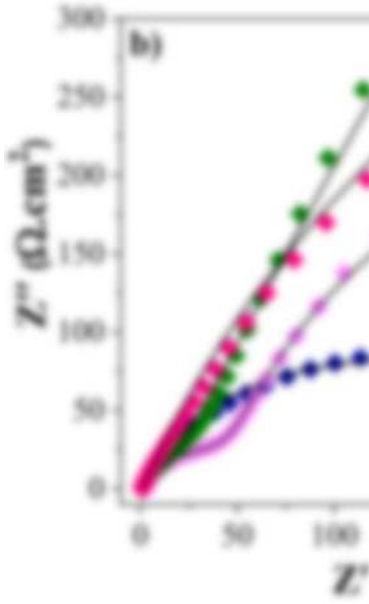
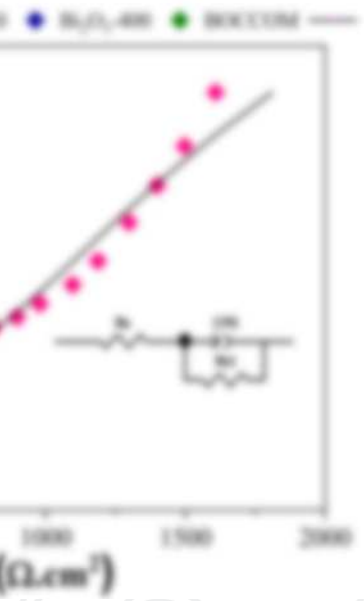


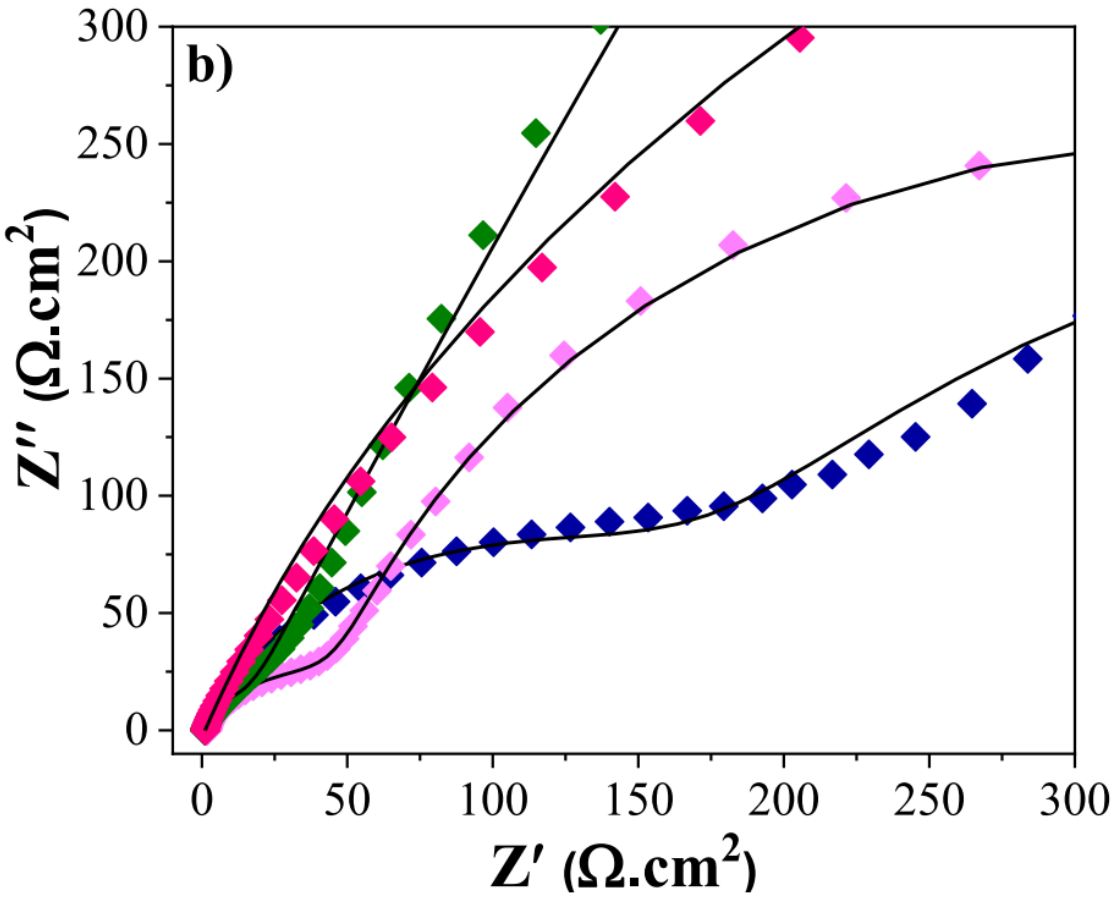
Fig. 4. Electrochemical impedance spectra of BOCCOM, BOC-90, BOC-150 and BOC-400 samples in 1.0 M KOH electrolyte (Nyquist plots); before electrolysis (A) and (B), and after electrolysis (C) and (D).

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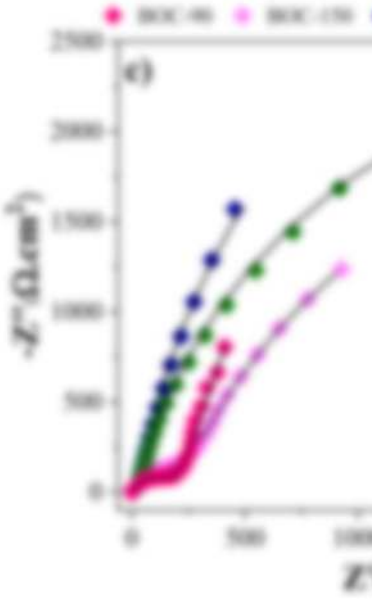


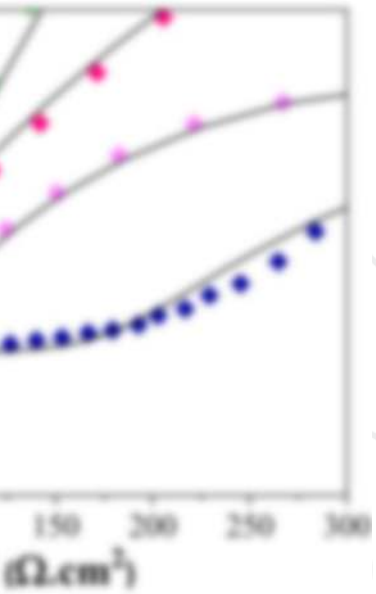
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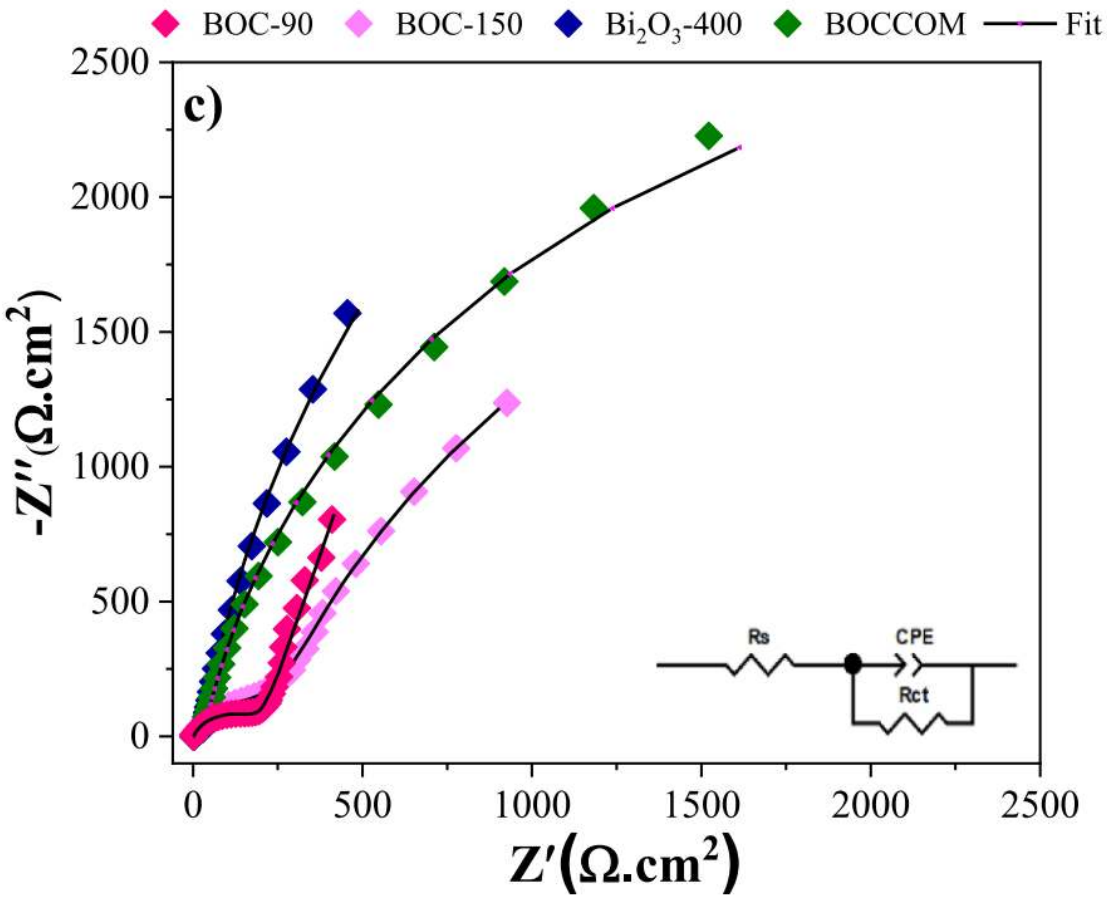
Selective electrochemical CO_2 reduction to formate at industrial current densities using 2D $Bi2O_2CO_3$ nanosheets

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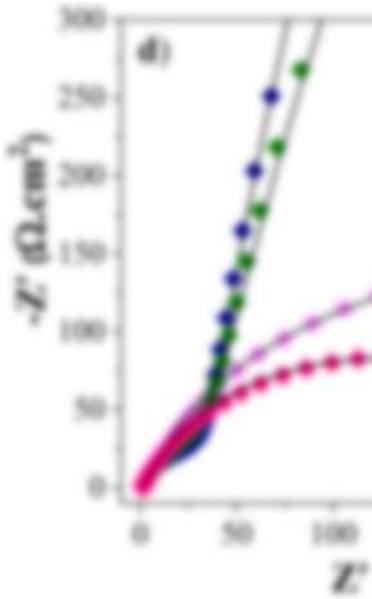


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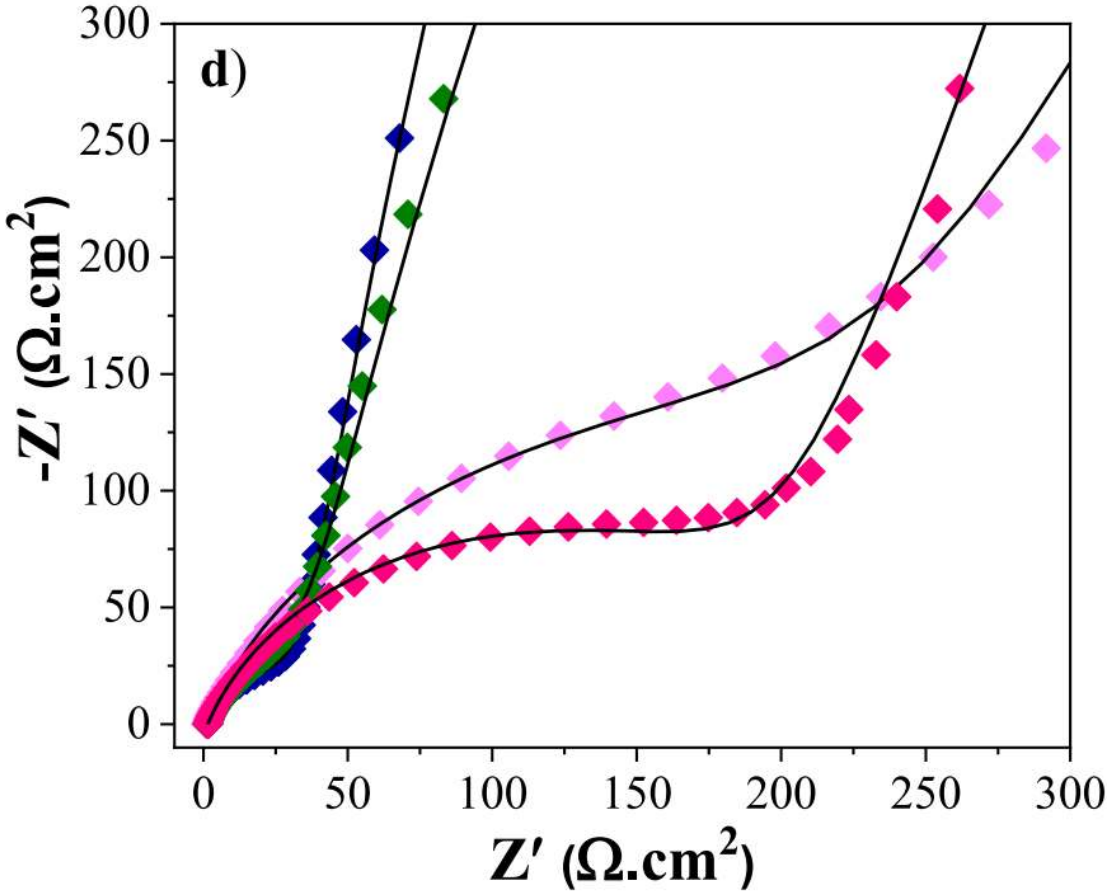
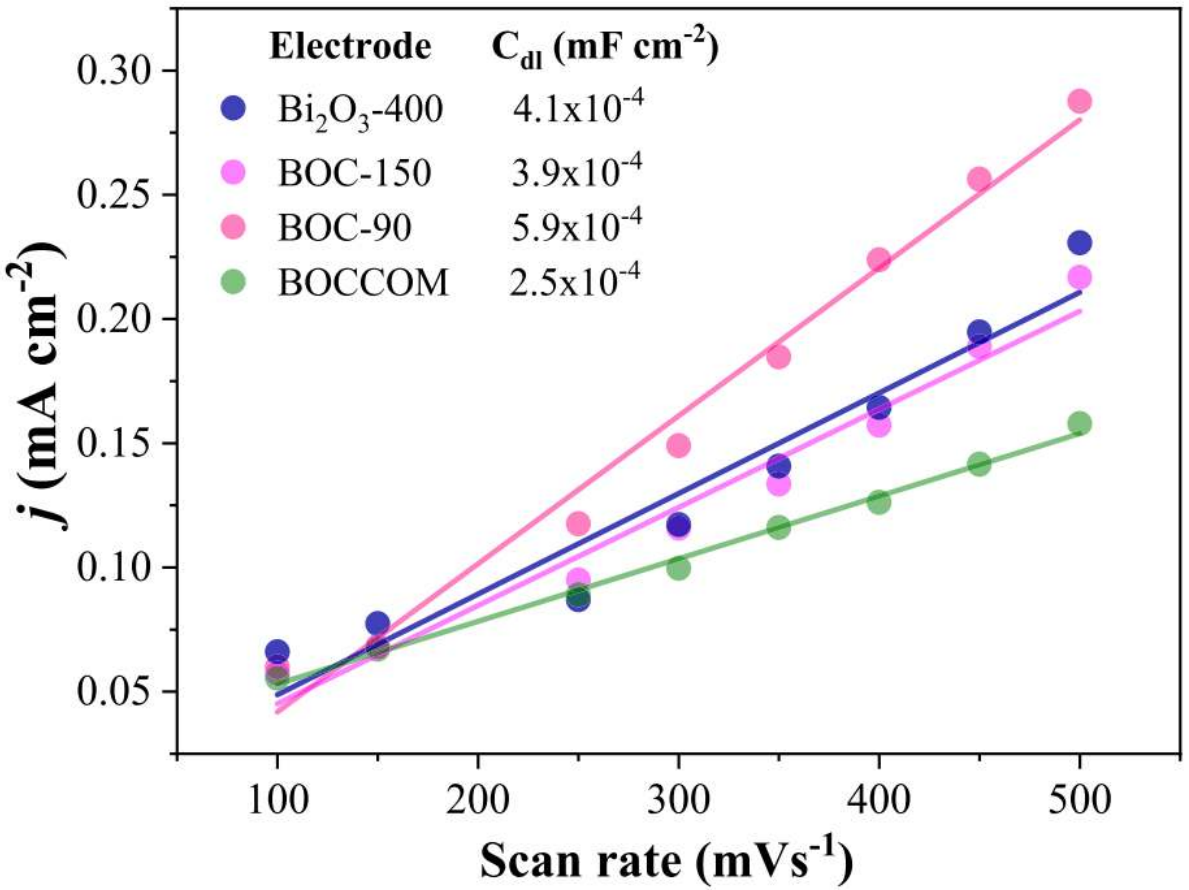


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3 – Caracterização Físico-Química





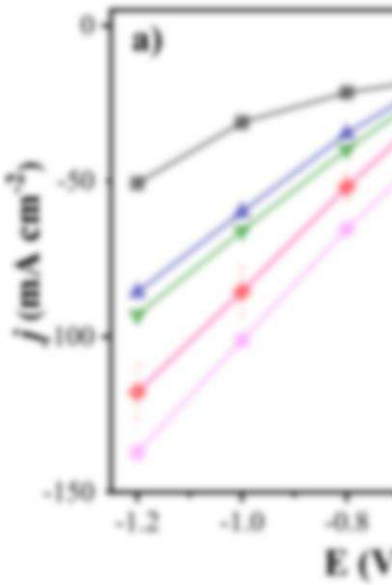


Fig. 5. Double-layer capacitance (C_{dl}) obtained by cyclic voltametry studies at different scan rates from 100 to 500 mVs^{-1} of BOCCOM, BOC-90, BOC-150 and Bi_2O_3–400 samples.

3 – Caracterização Físico-Química

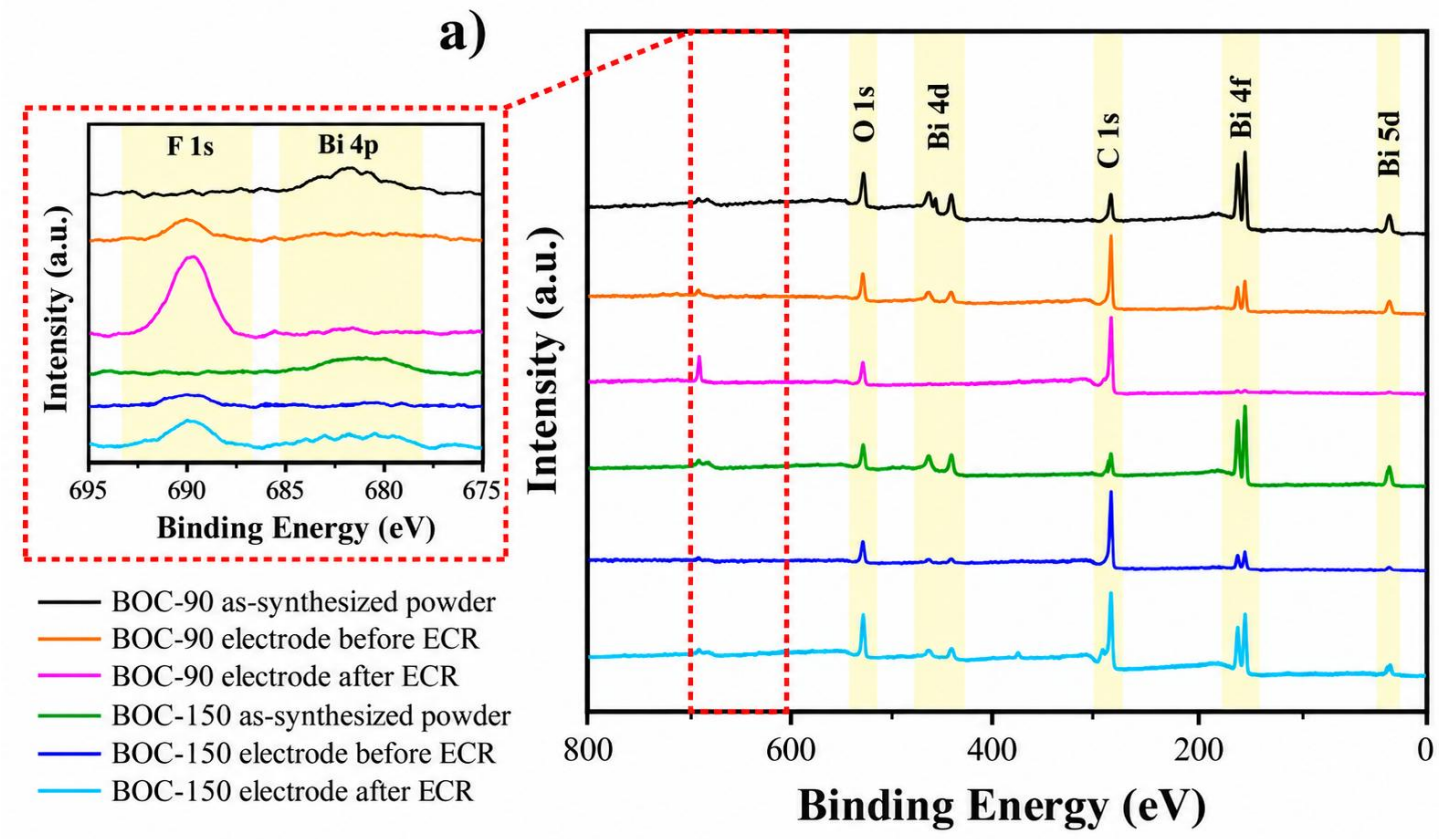


Fig. 6. a) XPS survey spectra of BOC-90 and BOC-150 powders (as-synthesized) and electrodes before and after the ECR reaction.

3 – Caracterização Físico-Química

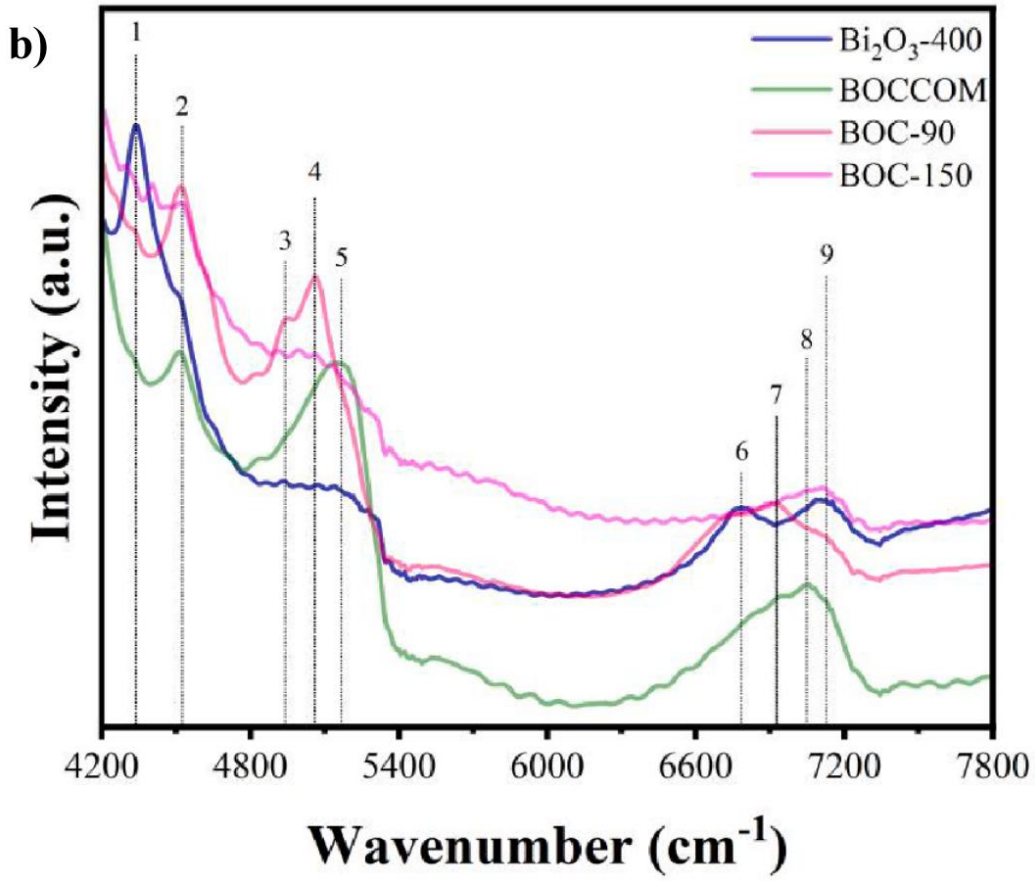


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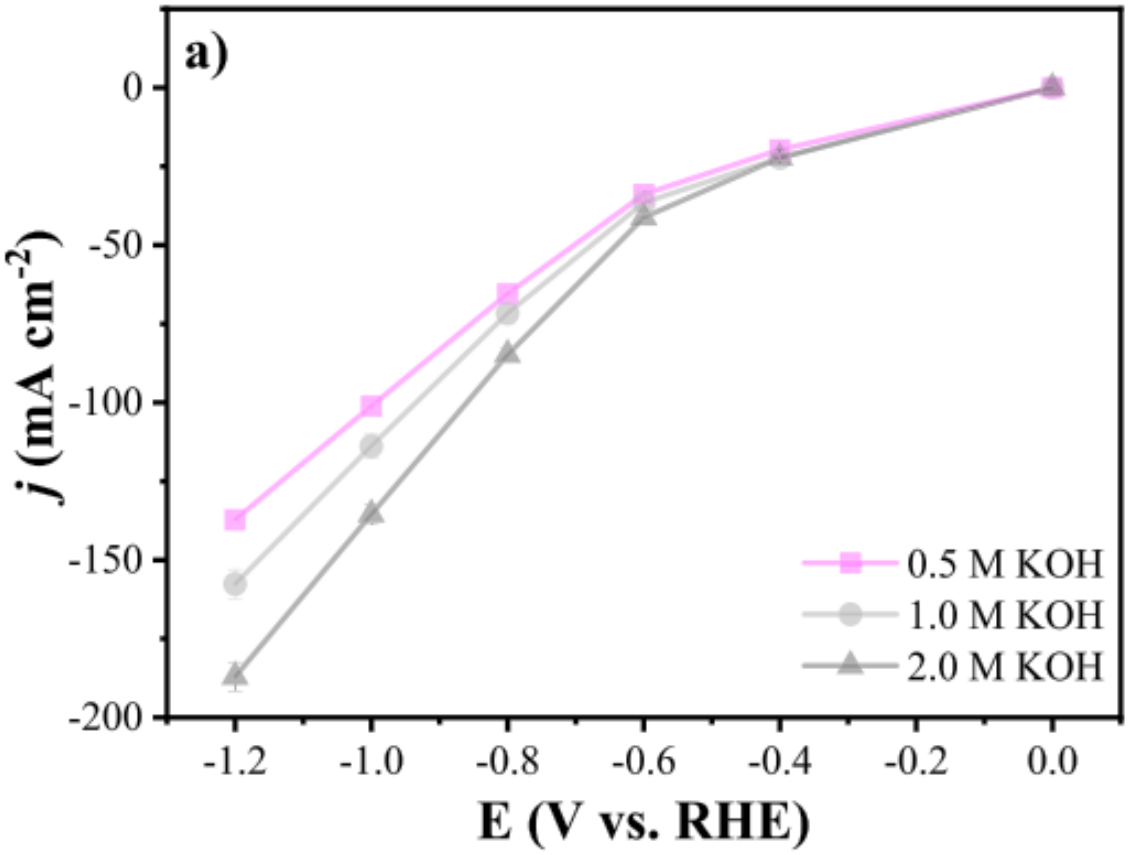


Fig. 7. (a,b) LSV curves and FEHCOO− of 50% BOC-150 at different KOH concentrations (0.5, 1.0, and 2.0 M); (c,d) LSV curves and FE of BOC-150 with different catalyst/carbon black ratios (50, 75, and 100%) after 30 min.

3 – Caracterização Físico-Química

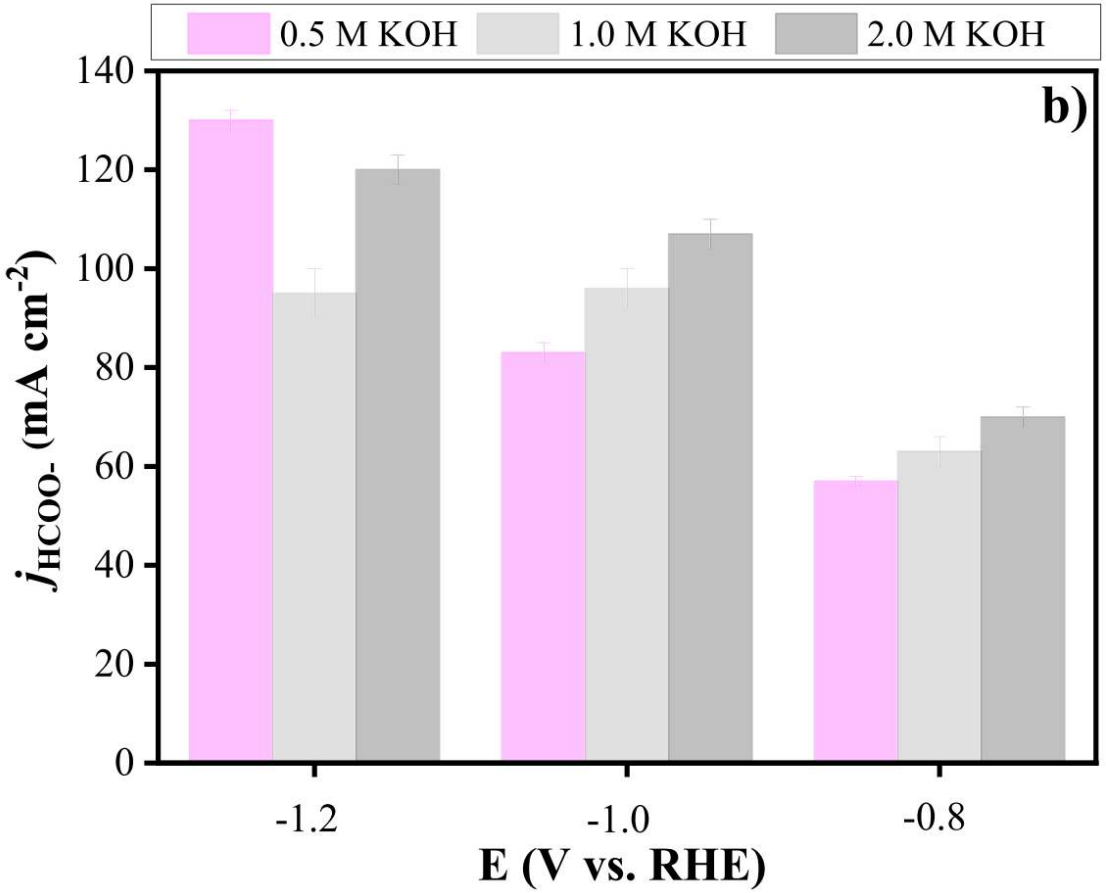


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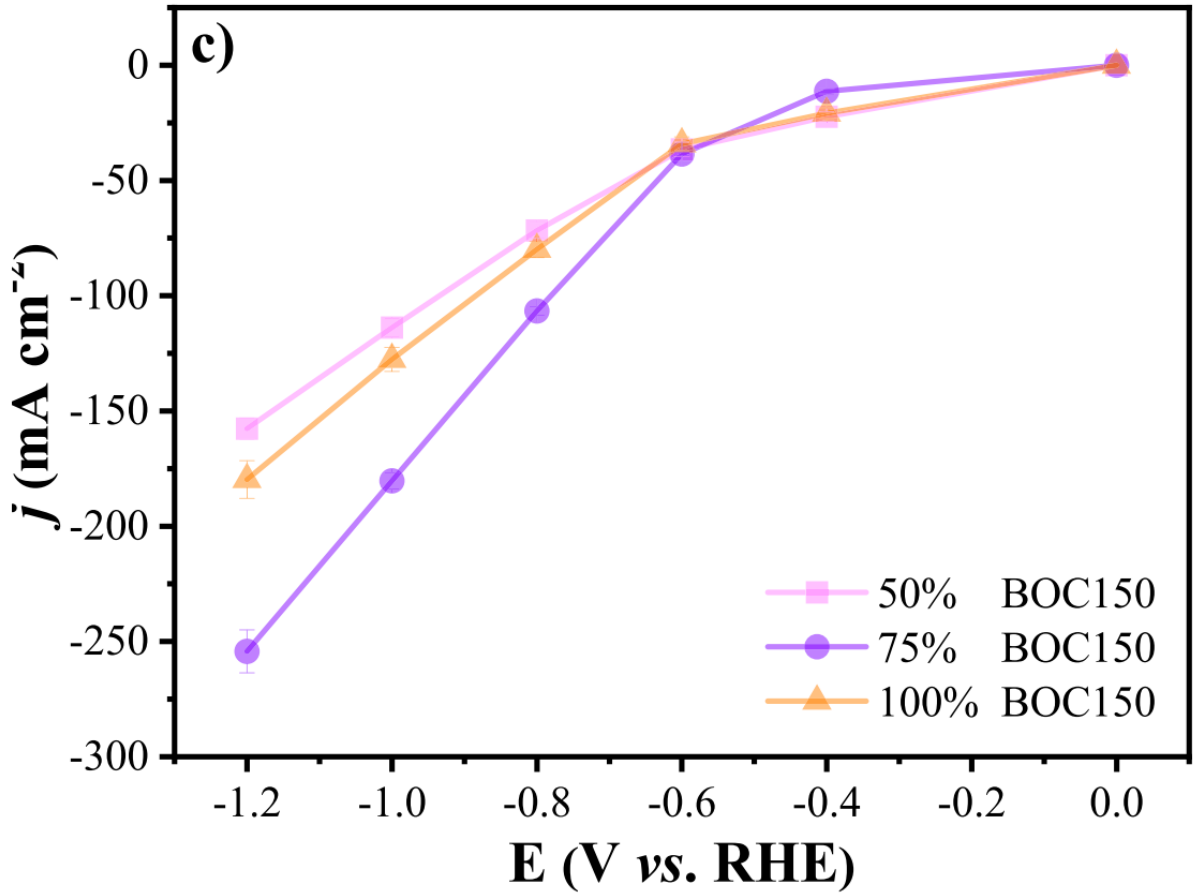


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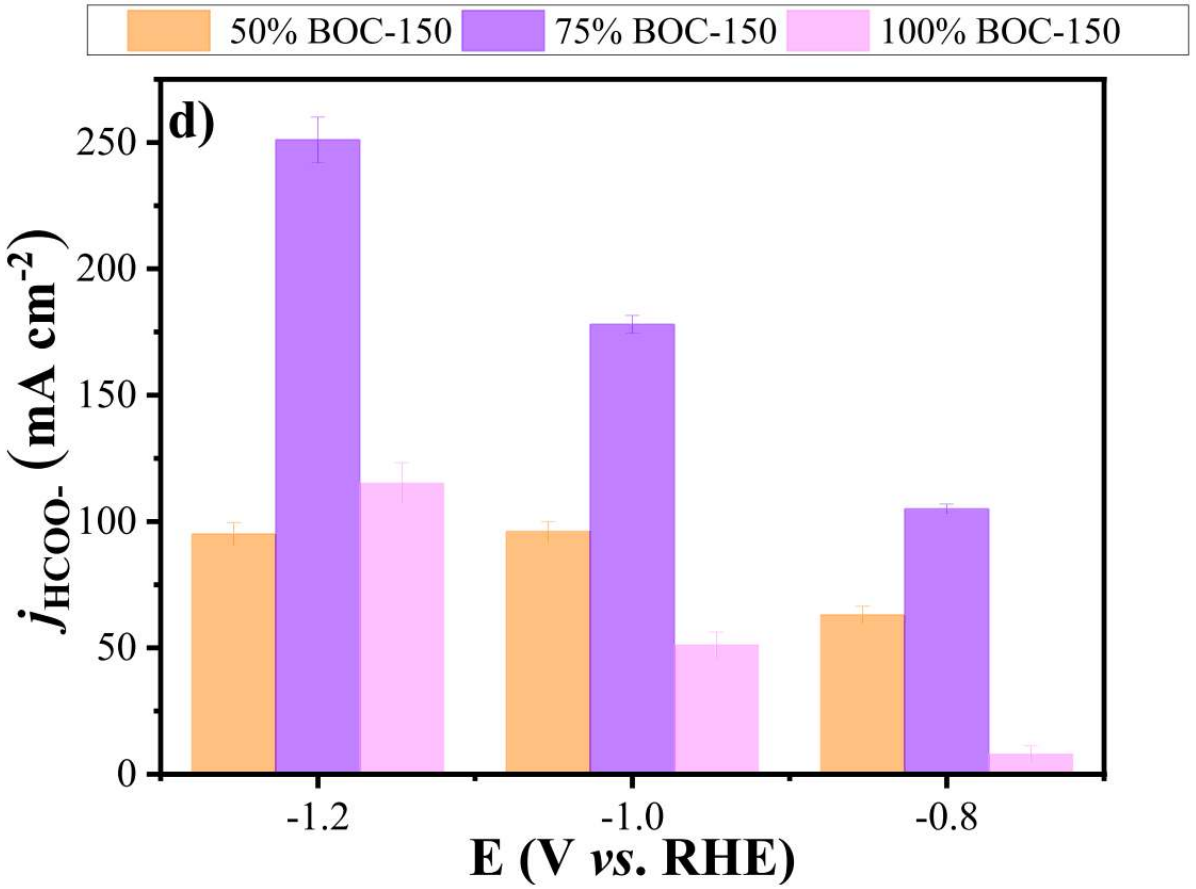


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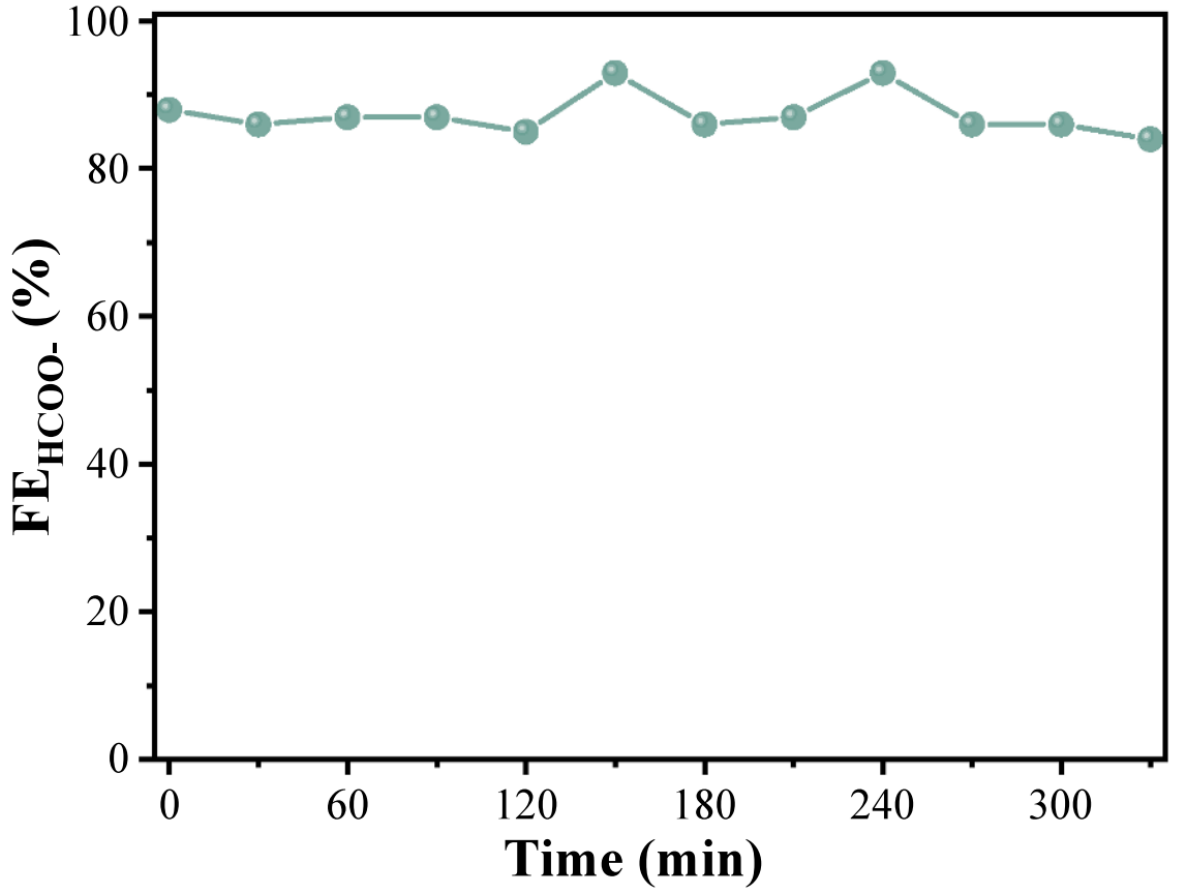
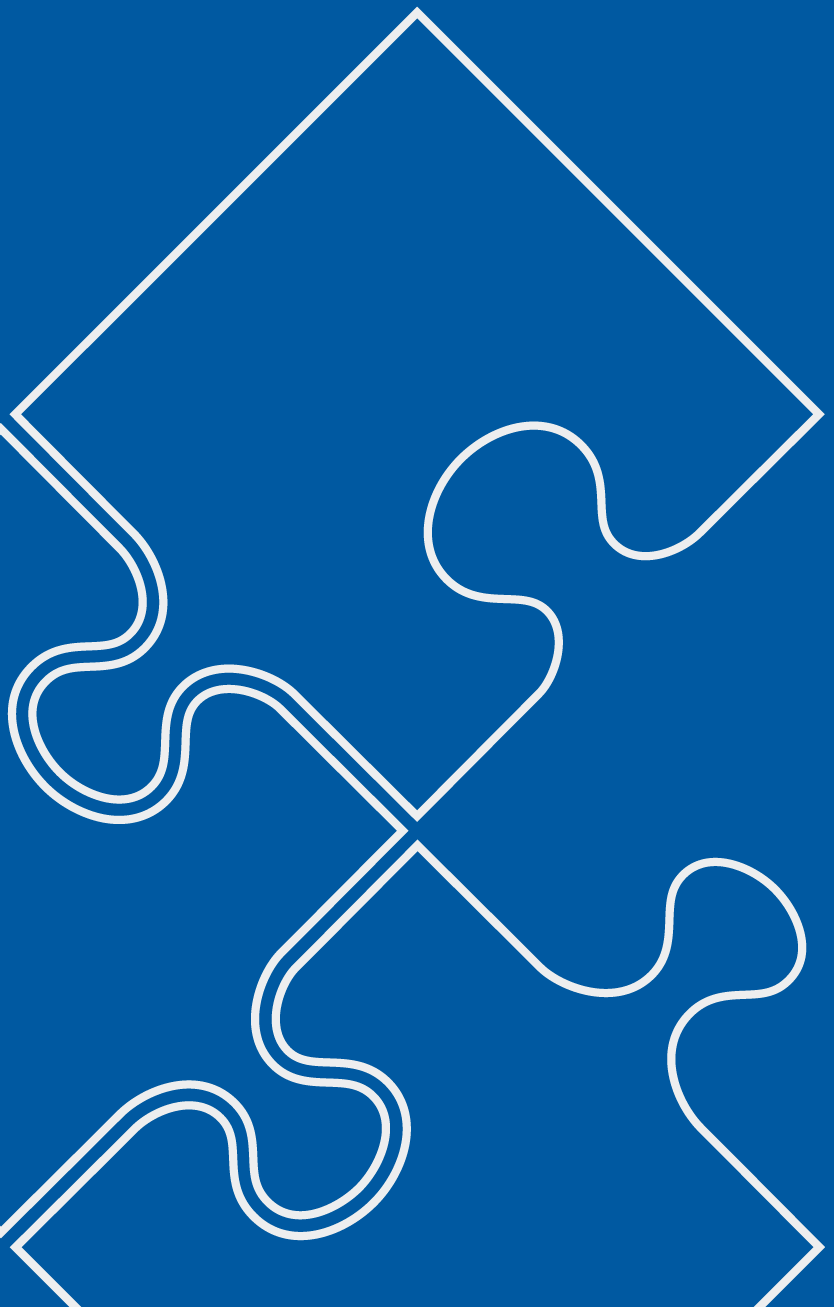


Fig. 8. Chronopotentiometric stability of the BOC150 catalyst at − 40 mA in 0.5 M KOH, showing FE_{HCOO-} over time.



#4

Conclusões

Considerações finais sobre o desempenho dos catalisadores

4 – Conclusão

Nessa condição, foram alcançados **$-250\ mA\ cm^{-2}$** e **$FEHCOO^-$ > 90%**.

BOC-150 foi o catalisador de melhor desempenho para a redução de CO_2 a $HCOO^-$.

A condição otimizada foi **1,0 M KOH com 75% BOC-150 e 25% carbon black**.

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4 – Conclusão

A **EIS indicou menor Rct para BOC-150**, sugerindo transferência de carga mais favorável.

O **NIR mostrou água fortemente adsorvida em BOC-90**, o que pode prejudicar a adsorção de CO_2.

O **XPS evidenciou menor estabilidade de BOC-90**, com perda de sinais de Bi após a ECR.

4 – Conclusão

O **BOC-150 em GDE de PTFE permaneceu estável por 6 h**, mantendo **$FEHCOO^-$ > 80%**.

O desempenho superior foi atribuído à **estrutura 2D, alta densidade de sítios ativos e facilidade de transferência de carga**.

Os resultados demonstram o **potencial do BOC-150 como eletrocatalisador para conversão de CO_2 a formiato em condições relevantes industrialmente**.

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