

Supporting Information

Exploring the Linear Relationship Between Potential Dynamics and Interfacial Capacitance: An Implications for Enhancing Turnover Frequency in Electrochemical Water Splitting

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This file contains 8 pages in which the details of Electrodes fabrications, material preparation for different characterizations, data for OER, comparative electrocatalysis datas are given in detail.

Number of Figure: 4

Number of Table: 1

EXPERIMENTAL

Methods and Materials

NiO powder catalyst was obtained from Sigma-Aldrich having an average size of about 225 nm. Hg/HgO reference electrode was purchased from CH Instruments Pvt. Ltd. DI water have been used for the whole electrochemical characterizations. The NiO modified carbon cloth (CC) was used as working electrode and a graphite rod has been used as counter electrode. The electrochemical analyzer AURT-M204 was used for all electrochemical characterizations.

Electrode Fabrications

Carbon cloth (CC) with total dimension of $1 \times 4 \text{ cm}^2$ has been pre-treated with acid solution to make it hydrophilic followed by washing with water ethanol mixture, The dried CC were then used as substrate electrodes. A catalyst ink of composition 750 μL water, 200 μL of absolute ethanol and 50 μL 5% Nafion solution was prepared by dispersing exactly 3 mg of the NiO powder. The resulted solution was sonicated for 10 min to make the solution to be homogeneous. The volume of coated ink 67.0 μL respectively to have the loadings of almost 0.2 mg/cm^2 . The catalyst used for **Figure 1a** is commercial RuO_2 materials with two different catalysts loading of 0.2 and 0.4 mg/cm^2 over carbon. Corresponding polarization information were acquired in 1M KOH solution with a scan rate of 5 mV/sec. The polarization information is 100% iR corrected manually with respect to solution resistance value of 1M KOH is 4.52Ω .

Electrochemical Characterization:

The electrochemical analyzer AURT-M204 has utilized for all electrochemical characterizations. The used Hg/HgO (1 M KOH) electrode used as reference electrode was purchased from CH instrument. The Pt wire was purchased from Alfa Aesar and has used as the counter electrode. Entire potential data that were collected by taking Hg/HgO as a reference electrode and later it was converted to reversal hydrogen electrode (E_{RHE}) scale by considering the Nernst equation of

$$E_{\text{RHE}} = E_{\text{ref}} + 0.059 \times 14 + 0.098 \quad (T = 303 \text{ K}) \dots\dots\dots \text{S1}$$

Determination of Surface concentration of Fe@Ni₃Se₄ from the redox features of CV:

Calculated area associated with the reduction of Ni³⁺ to Ni²⁺ = 0.000906 VA

Hence, the associated charge is = 0.000906 VA / 0.01 Vs⁻¹

$$= 0.0906 \text{ As}$$

$$= 0.0906 \text{ C}$$

Now, the number of electron transferred is = 0.0906 C / 1.602 × 10⁻¹⁹ C

$$= 5.65 \times 10^{17} \text{ C}$$

Since, the reduction of Ni³⁺ to Ni²⁺ is a single electron transfer reaction, the number electron calculated above is the same as the number of surface-active sites.

Hence, the number of Ni participate in OER is = 5.65 × 10¹⁷ C

Determination of Turnover Frequency (TOF) from OER Current Density TOF in our study was calculated assuming that the surface-active Ni atoms that had undergone the redox reaction just before onset of OER only participated in OER electrocatalysis. The corresponding expression is,

$$TOF = \frac{j \times N_A}{F \times n \times \tau} \dots\dots\dots \text{S2}$$

Where, j = current density, N_A= Avogadro number, F = Faraday constant, n = Number of electrons and τ = Surface concentration.

Hence, we have,

$$TOF_{1.55 \text{ V}} = \frac{(1.19 \times 10^{-3}) \times (6.023 \times 10^{23})}{(96485) \times (4) \times (5.65 \times 10^{17})} = 0.00328 \text{ sec}^{-1}$$

S. No	Redox area (VA)	Scan Rate (mV/sec)	Charge (C)	ECAS	J (mA/cm²)	TOF (sec⁻¹)
1	0.000906	10	0.0906	5.65	1.19	0.0032
2	0.00138	20	0.069	4.30	1.19	0.0043
3	0.0017	30	0.056	3.53	1.19	0.0052
4	0.00192	40	0.048	2.99	1.19	0.0061
5	0.00211	50	0.0422	2.63	1.19	0.007
6	0.00226	60	0.0376	2.35	1.19	0.0078
7	0.00238	70	0.034	2.12	1.19	0.0087
8	0.00248	80	0.031	1.93	1.19	0.00959
9	0.00257	90	0.028	1.78	1.19	0.0104
10	0.00265	100	0.0265	1.65	1.19	0.0112

Table S1: Details electrochemical results.

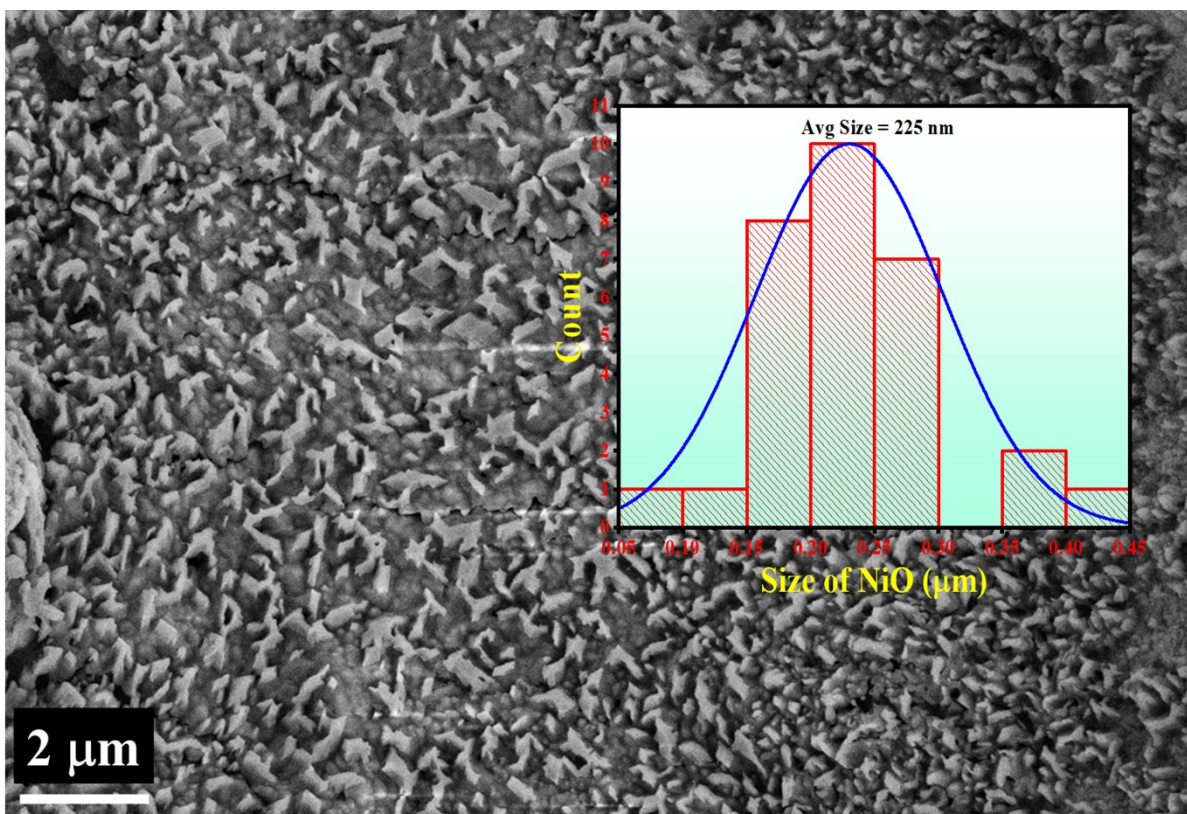


Figure S1: Scanning electron microscopic (SEM) image of the NiO over carbin cloth and inset of the figure shows corresponding size distribution of the particles.

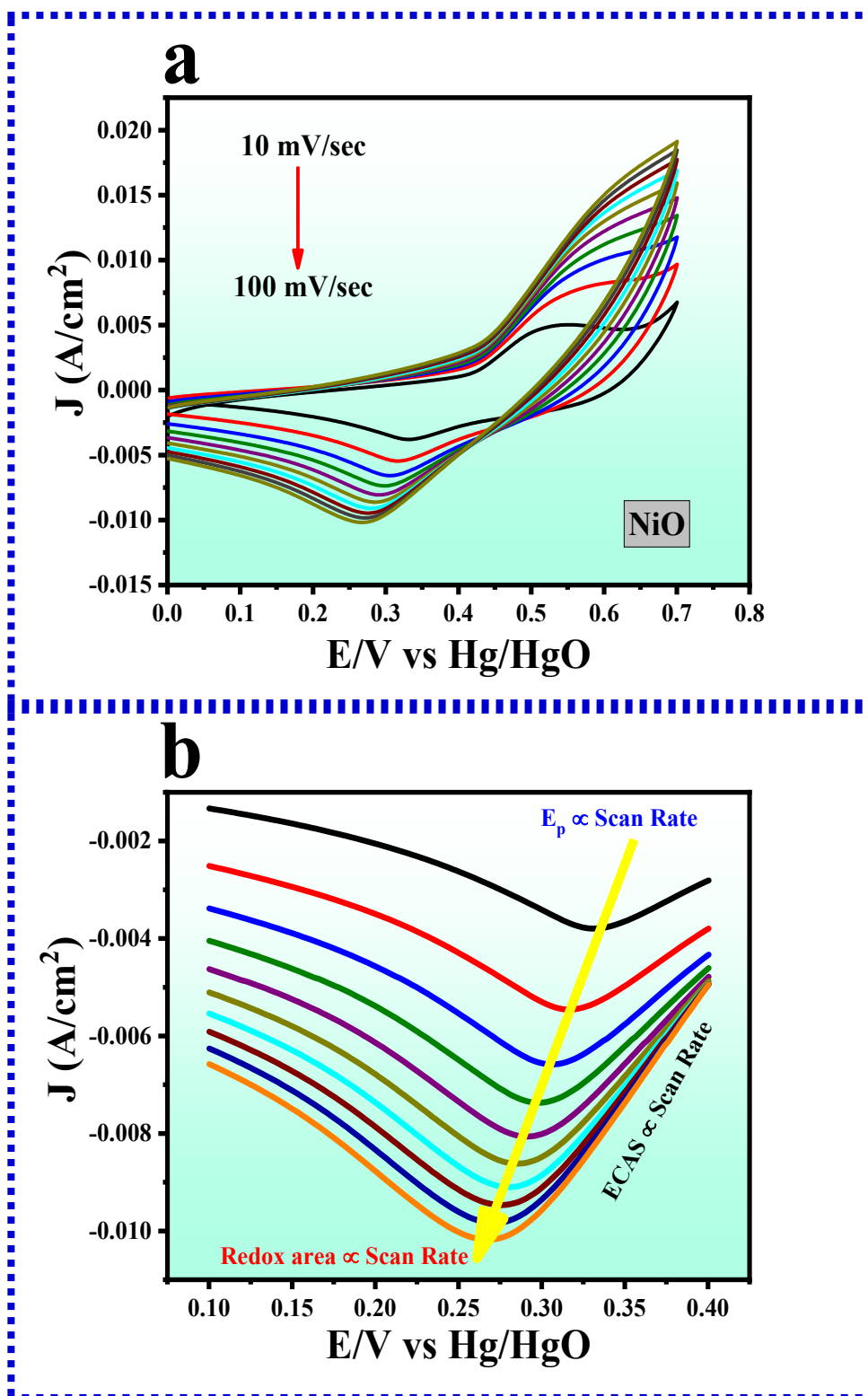


Figure S2: (a) Acquired CV of NiO modified working electrode with various scan rate values and (b) corresponding redox integration information with respect to various scan rates.

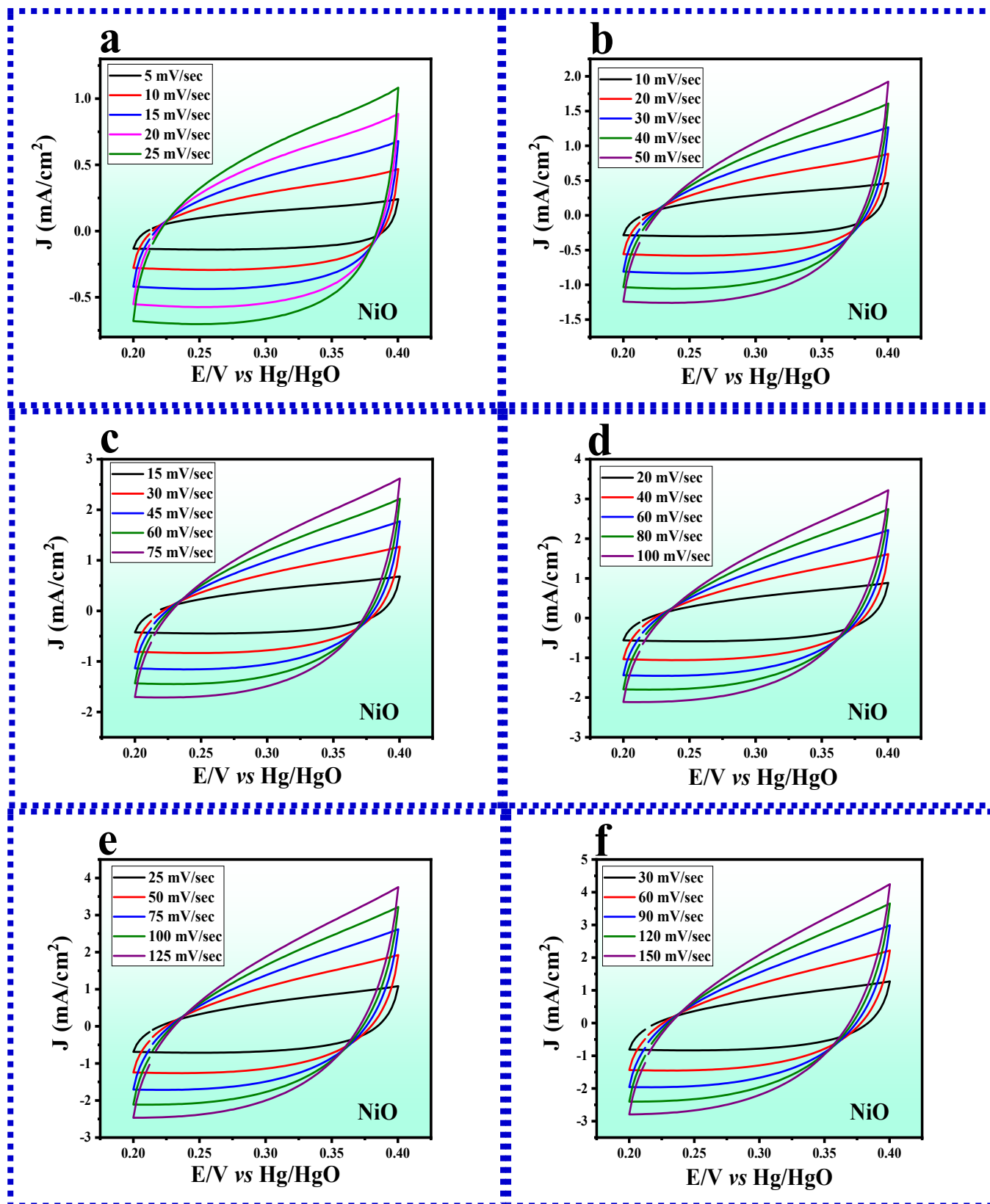


Figure S3: (a-f) Scan rate dependent CV information in the non-faradaic region of OER polarization curve with various scan rate difference.

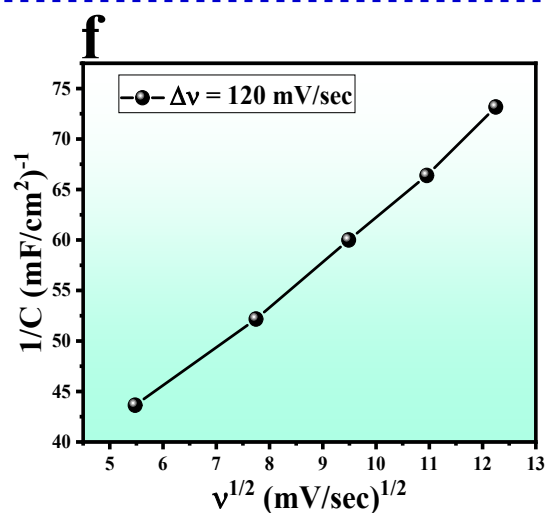
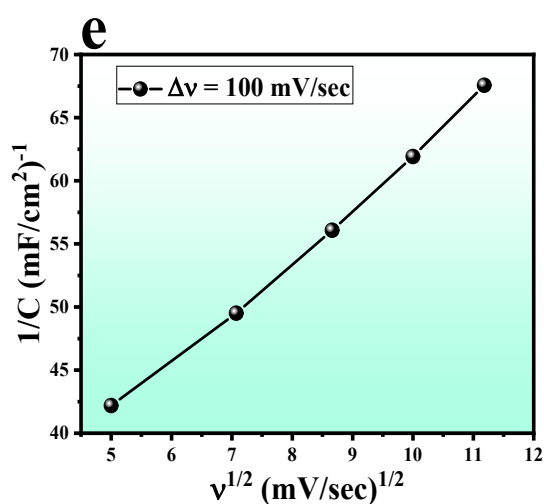
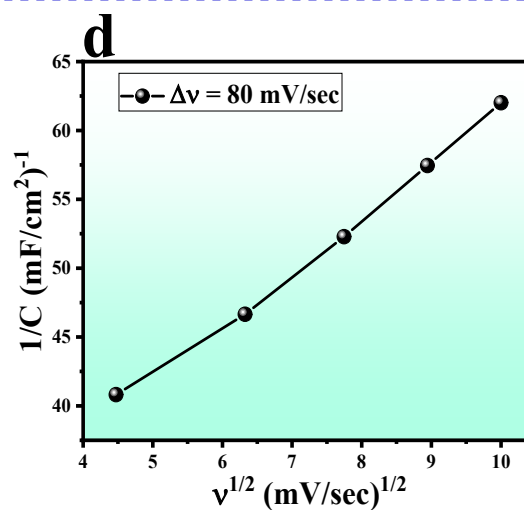
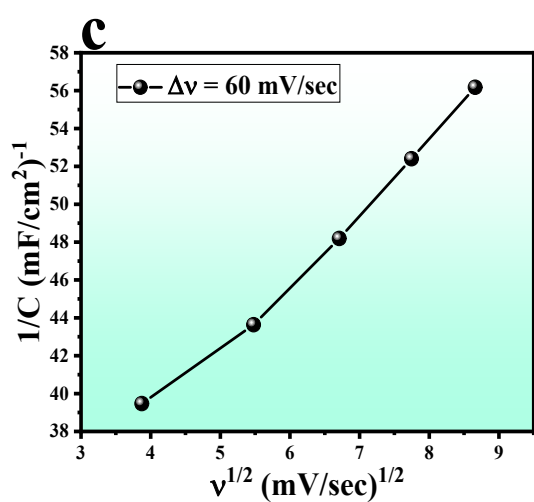
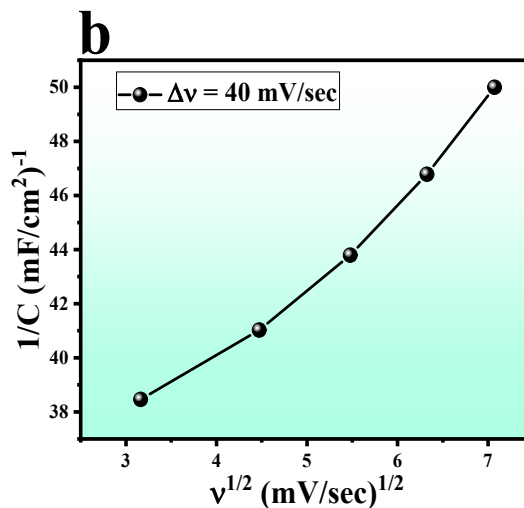
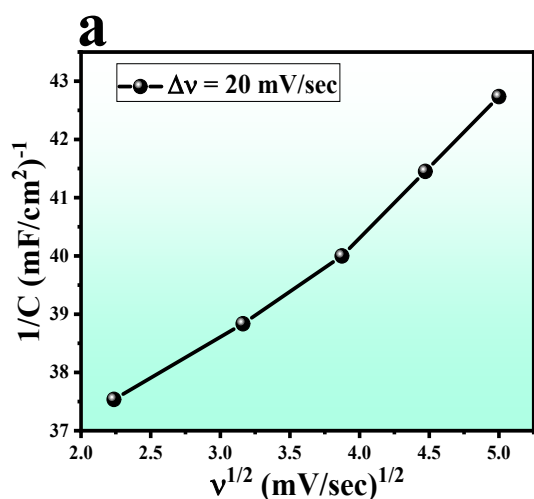
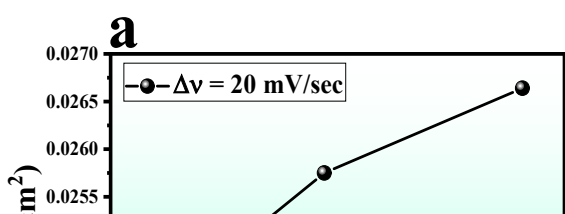


Figure S4: (a-f) $1/C$ vs $(\text{scan rate})^{1/2}$ plots for different Δv values (Δv represent the difference in initial selected scan rate value and final one as can be seen from the **Figure S2**).



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