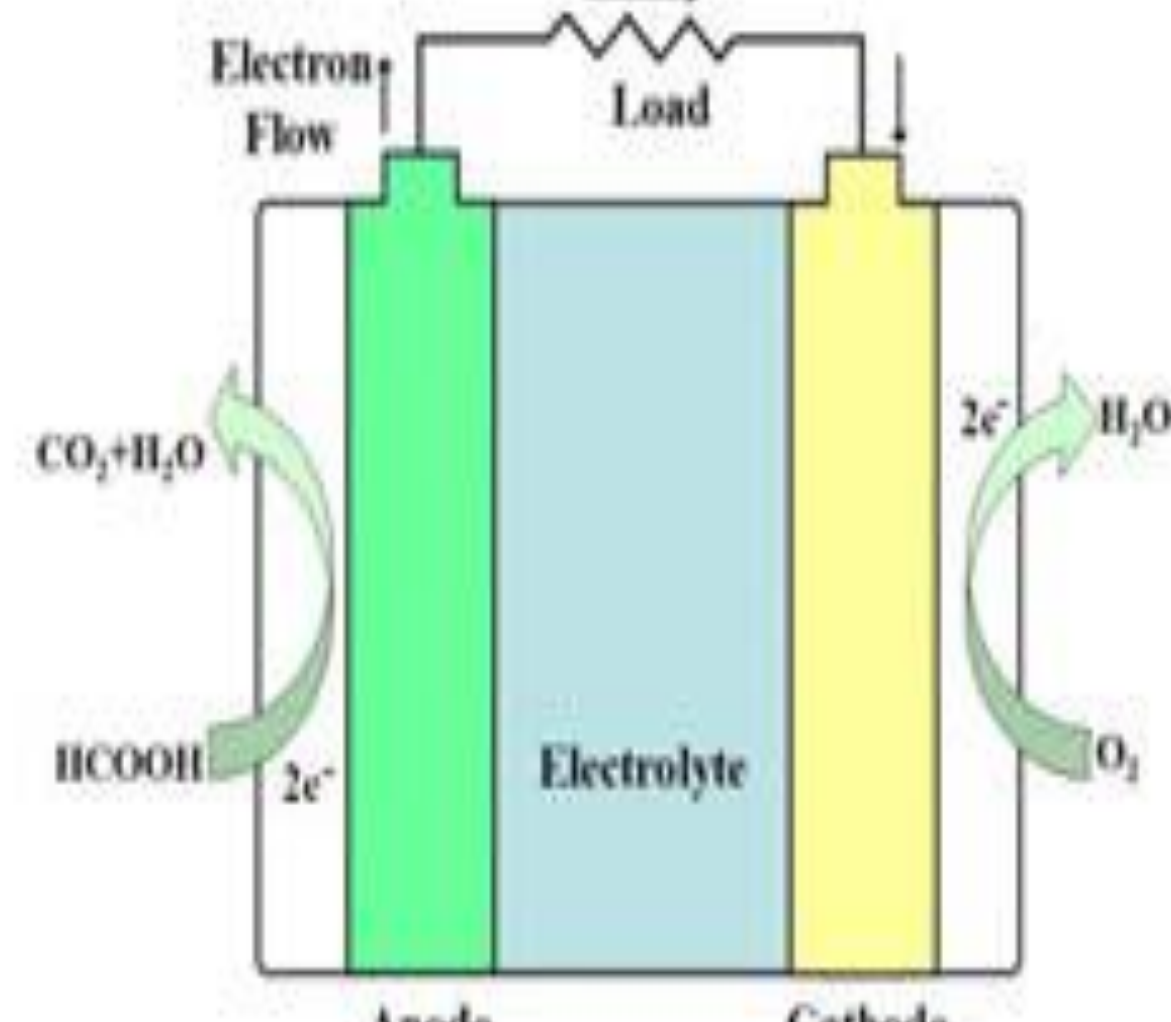




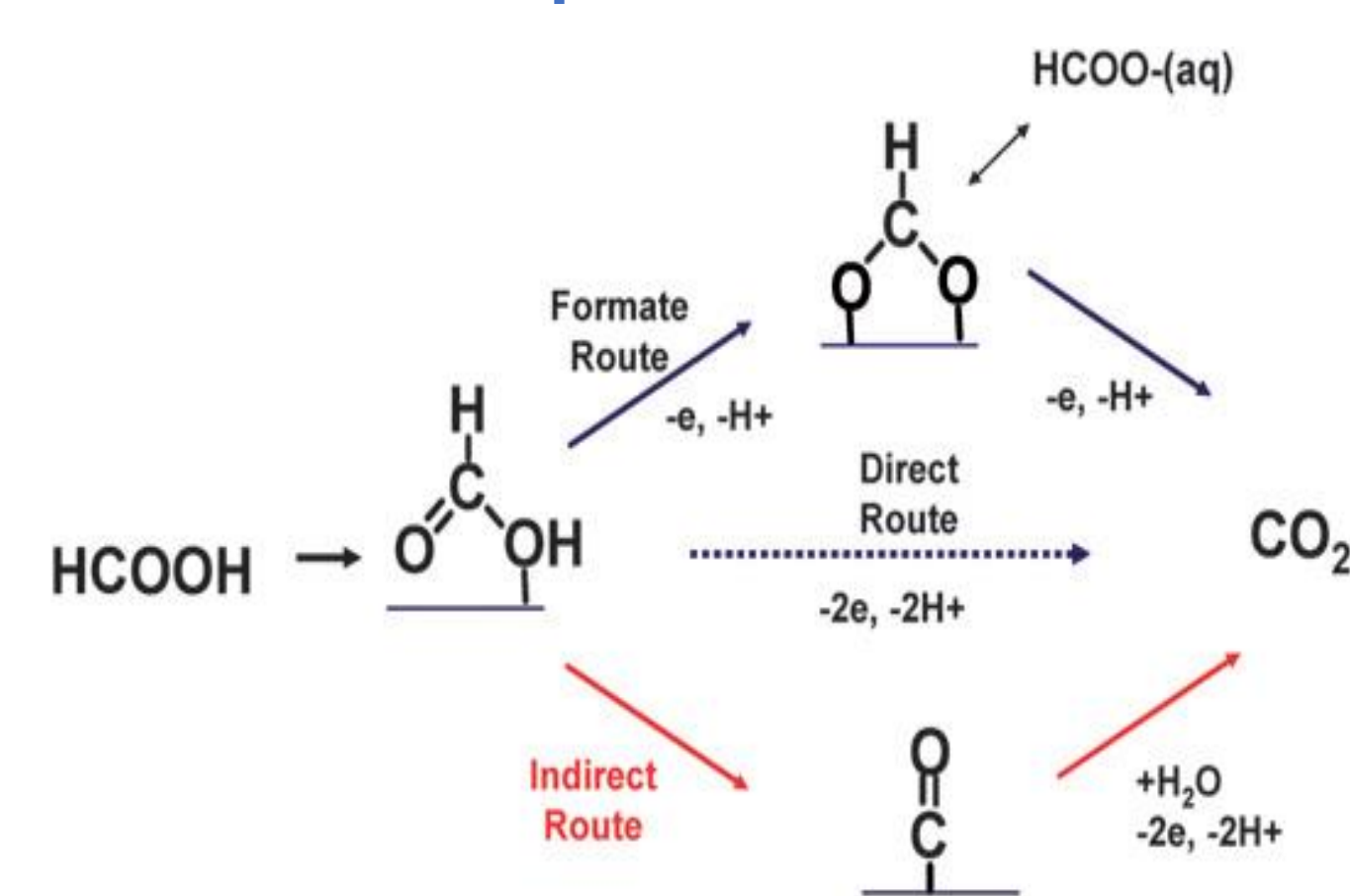
Summary

- ❖ The influence of various parameters affecting electrocatalytic oxidation of formic acid on Pd/WC electrodes is examined, and the optimum conditions are provided.
- ❖ The synthesized electrodes have satisfactory stability and improved activity
- ❖ The electrochemical behavior toward formic acid oxidation (FAO) are compared to that on WC, Pd(111), and polycrystalline Pt.
- ❖ The base cyclic voltammograms of Pd/WC and its electrochemical performance toward FAO are quite similar to that of pc-Pt, but differs greatly from that of Pd(111).
- ❖ FAO activity reaches 150 mA/mg Pd at 0.45 V vs RHE.
- ❖ The results indicate that Pd/WC nanocatalysts with ultra-low Pd loading synthesized by ALD may serve as efficient Pt-like electrocatalysts.

Working principal of Direct Formic Acid Fuel Cell



The reaction paths involved in the electro catalytic oxidation of formic acid to CO2



- ❖ It is one of the promising clean energy conversion technology

- ❖ Pd is cheap and rich in reserve

- ❖ Pd based catalyst increases the catalytic activity of formic acid oxidation and no (or less) poisoning CO intermediate formed!

- There is no consensus on the mechanism and intermediate for FAOR and key factors which controls FAOR activity

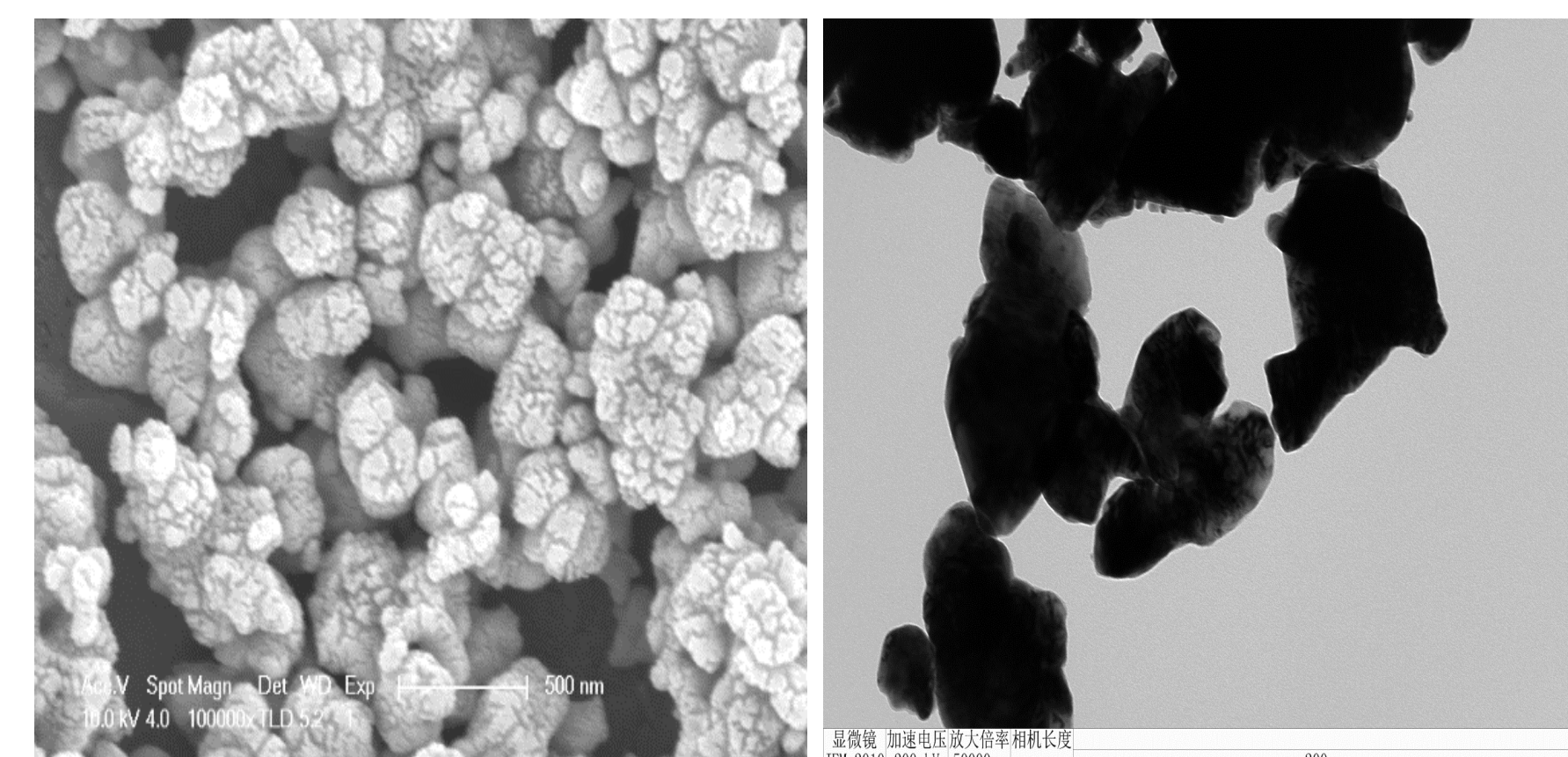
- Study the oxidation of FAOR intermediates will be of great help to improve the understanding of the above issues.

2. Experiments

- ❖ To synthesize Pd/WC with different layers, Atomic Layer Deposition (ALD) is used.
- ❖ The physicochemical properties of the as-prepared catalysts are characterized by XRD, Raman spectroscopy, SEM, EDS, XPS, and ICP.
- ❖ Chronoamperometry and cyclic voltammetry are used to investigate the activity of electrocatalyst

3. Results and Discussion

SEM and TEM images of the WC/Pd nanoparticles

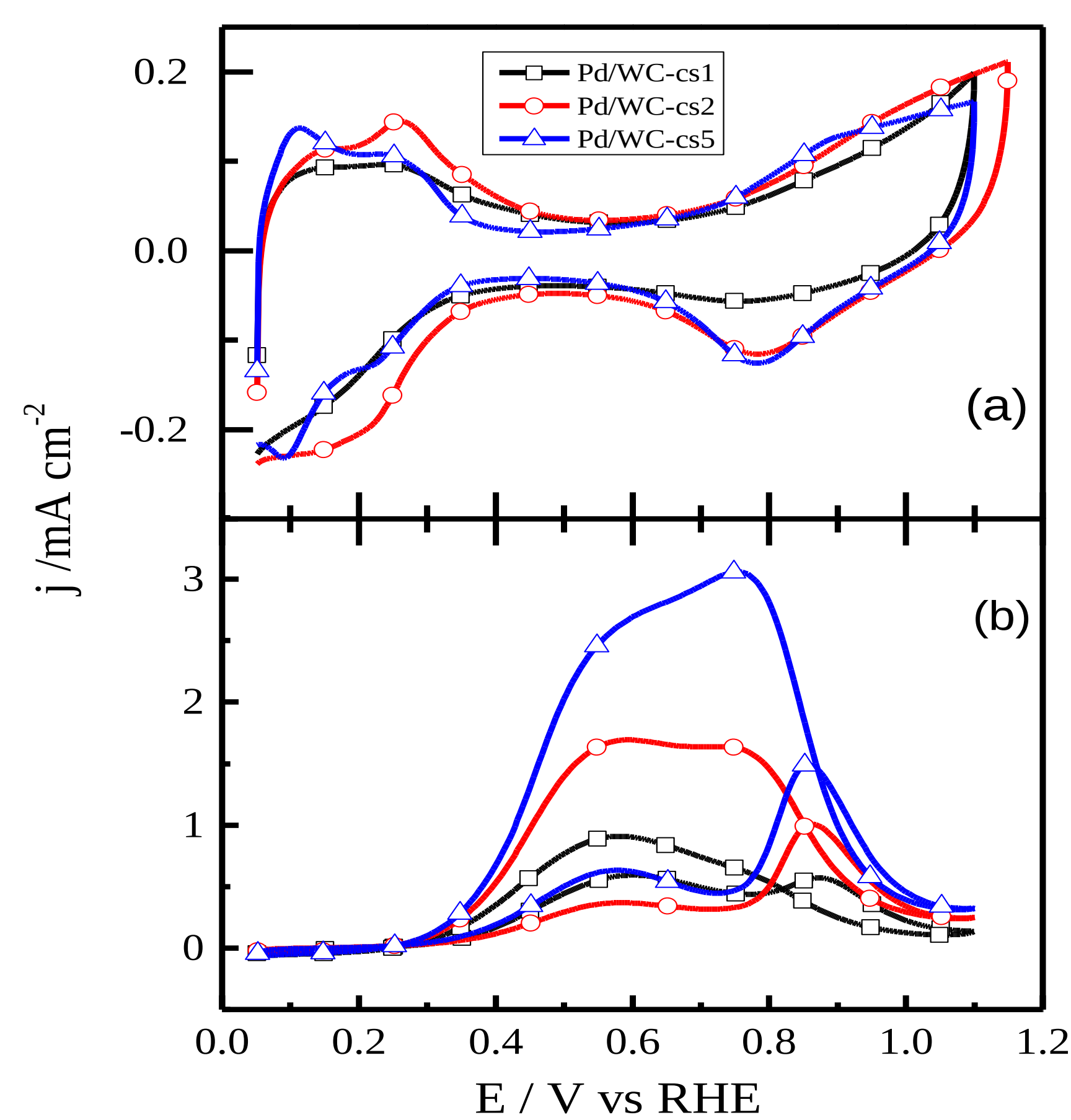


- ✓ WC NPs are of irregular shape with particle size in the range of 50 to 400 nm

- ✓ Top surface of the WC small nanoparticles are composed of NPs with diameter of a few nanometers

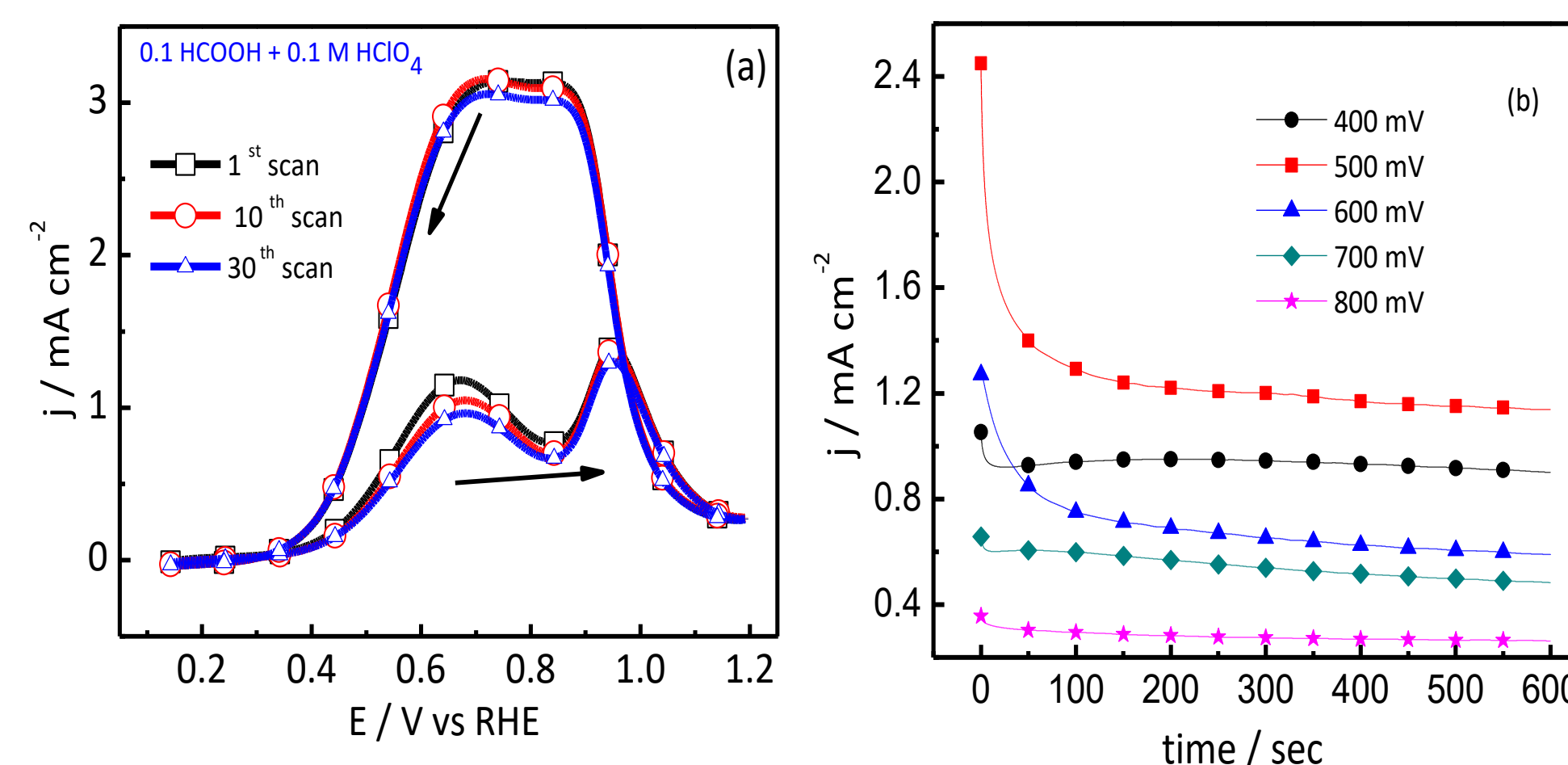
- ✓ No detection of Pd nanoparticles.

Formic Acid on WC supported Pd Nanocatalysts Prepared by ALD



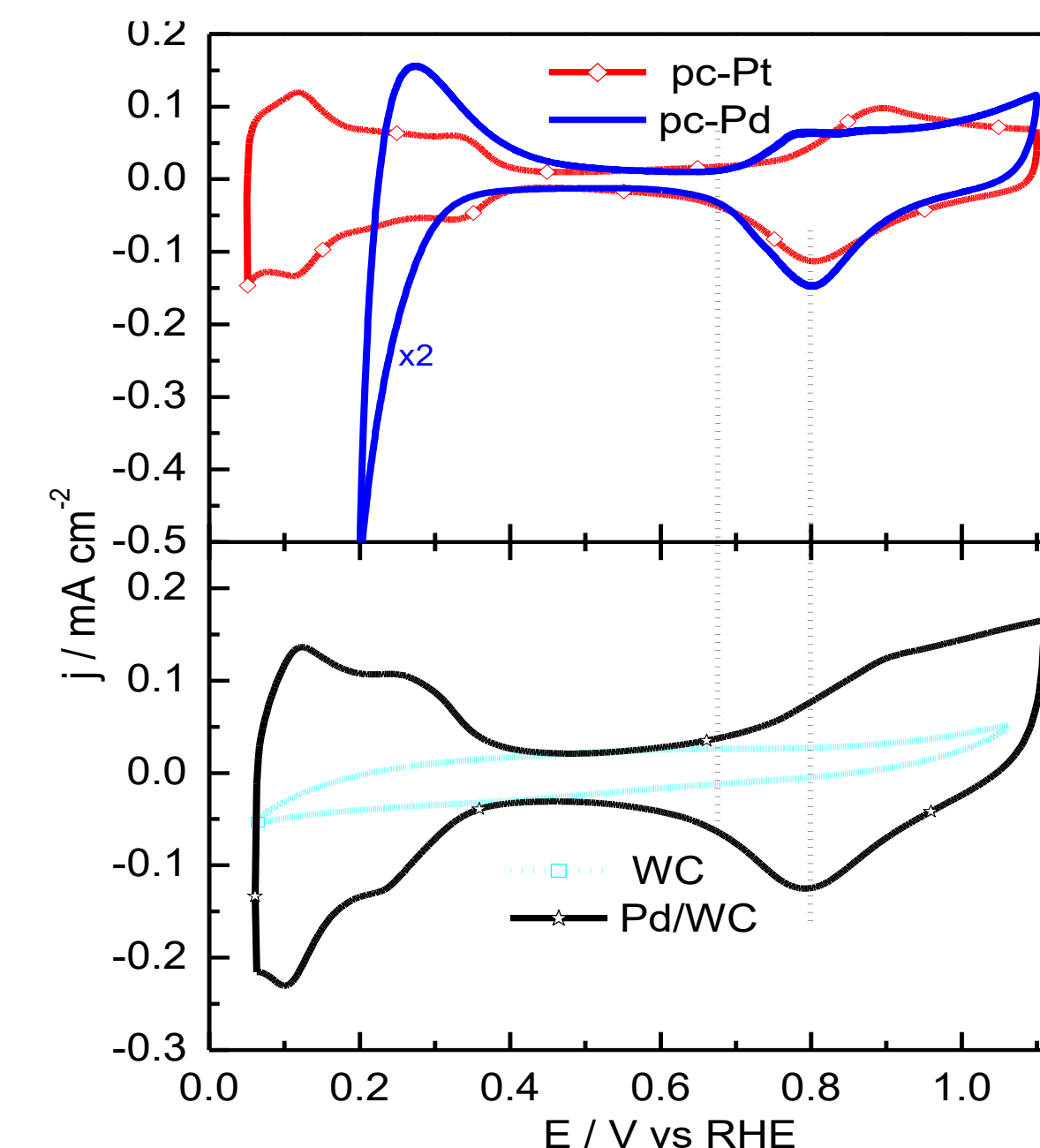
- ✓ The electrochemical surface area are 0.3, 0.31 and 0.36 cm² for Pd/WC (CS1), Pd/WC (CS2) and Pd/WC (CS5). CS: Cycle
- ✓ FAO on WC/Pd electrocatalysts have similar characteristics to that on pc-Pt.
- ✓ WC deposited with Pd for five cycles displays largest FAO activity.

Testing the durability of Pd/WC (CS5)



- ✓ Peak current density does not decrease too much with continuous cycling
- ✓ The maximum current density, 1.3 mA cm⁻² appears at 0.5 V, at higher E, the current decays, due to the formation of PdO_x and W_xO_y

Cyclic voltammogram of Pd/WC (CS5)

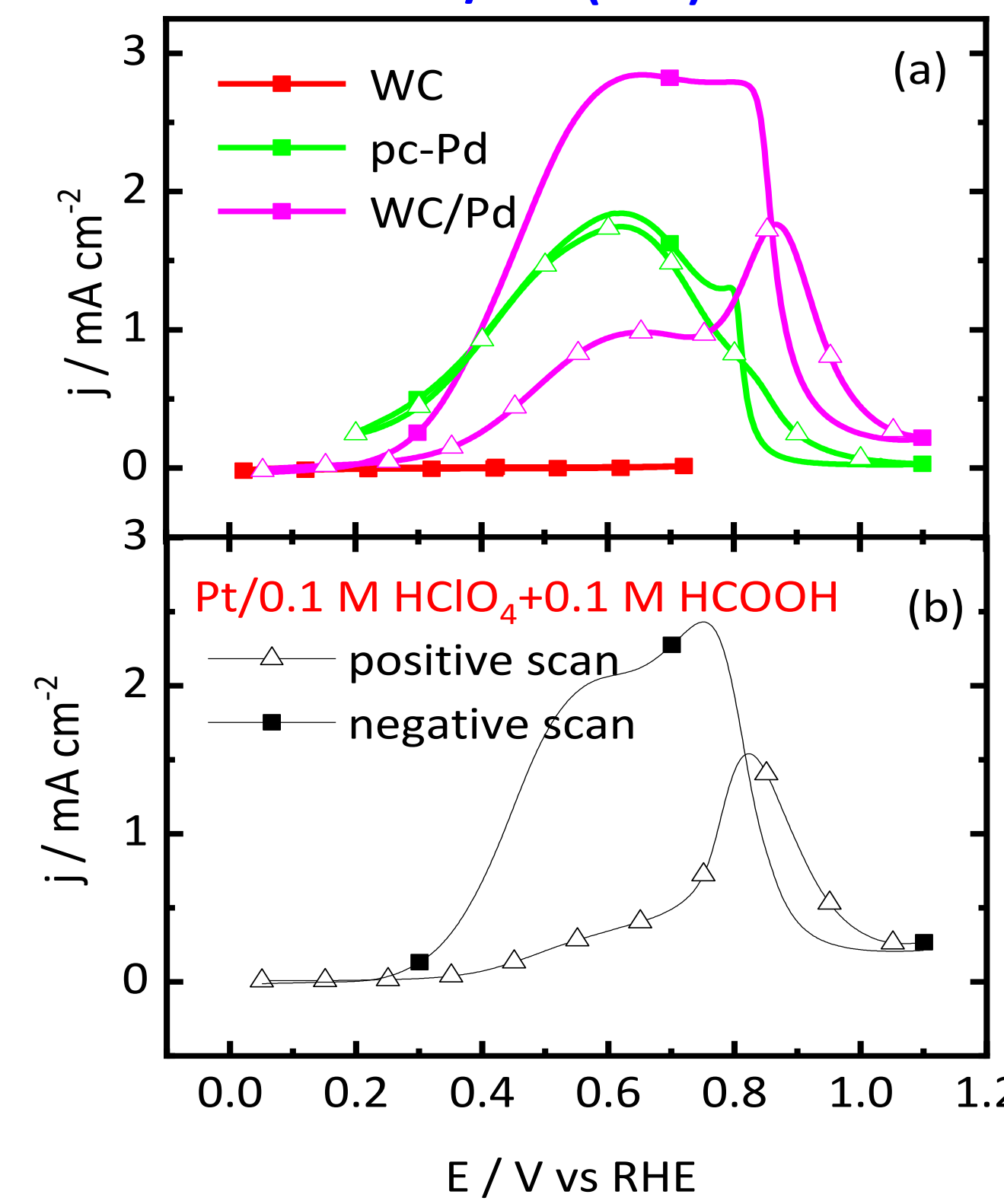


- ❖ Displays the cyclic voltammograms for WC and Pd/WC in 0.1 M HClO₄.

- ❖ For comparison, the base CVs for Pd(111) and polycrystalline Pt recorded under exactly the same conditions are also included in the top panel.

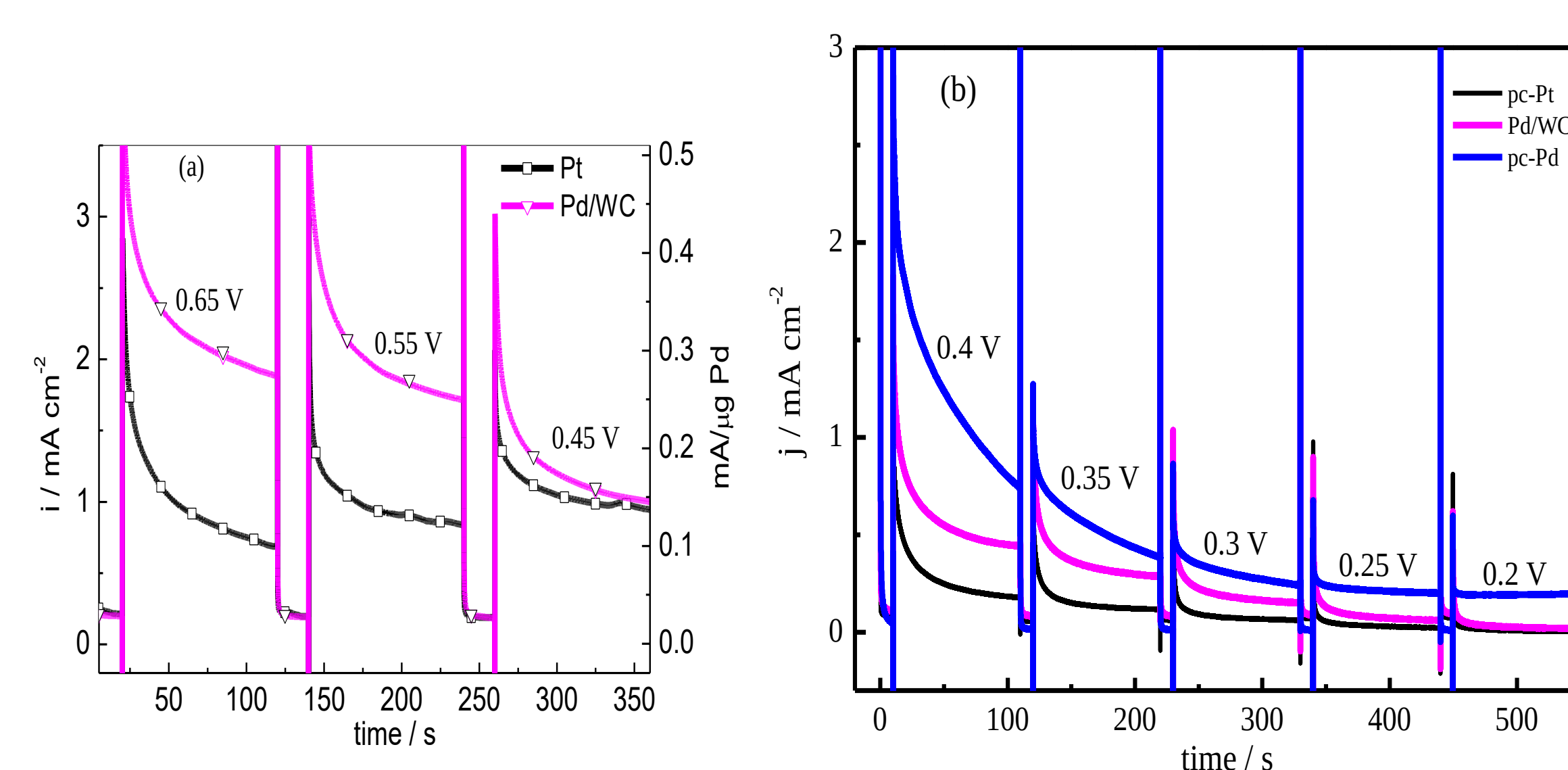
- ❖ There is barely no redox peak for WC in the potential regime from 0 to 1 V.

Comparison of FAO on Pd/WC (CS5) and Other catalysts (pc-Pt, pc-Pd)



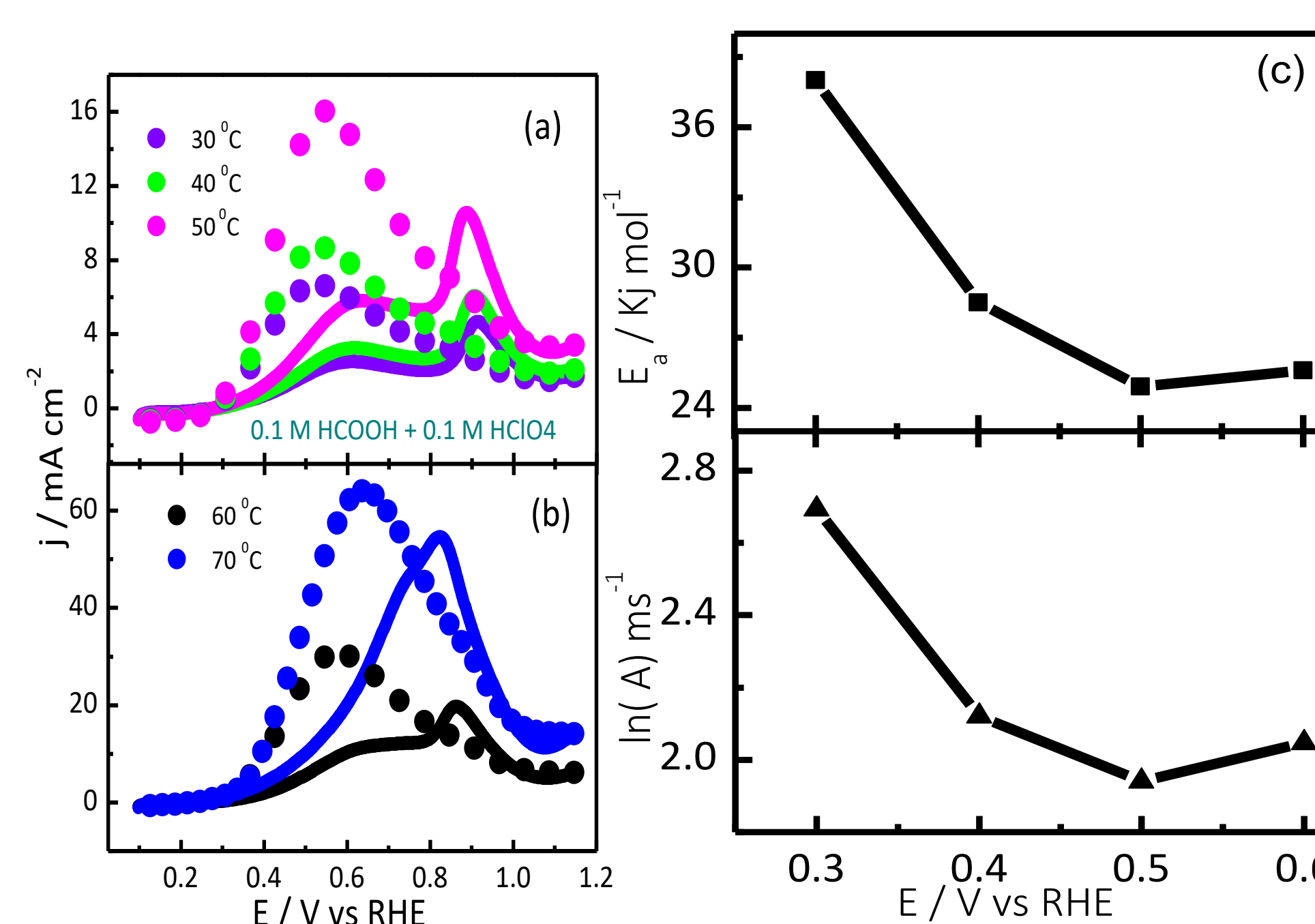
- ✓ pc-Pt and Pd/WC display similar potential dependence, and FAO activity on both electrodes are comparable

Arrhenius Plots for Formic Acid Oxidation on Pd/WC Electrode



- ✓ The pc-Pd current density is greater than pc-Pt and Pd/WC current density
- ✓ The current density decreases with the applied potential
- ✓ At 0.2 V, the current density of pc-Pt and Pd/WC is the same.

Temperature Effect on Formic Acid Oxidation on Pd/WC Electrode



- ✓ The maximum current in the backward scan at 70 °C is ca. 10 times higher than that at 30 °C
- ✓ The deviation of the FAO current in the positive scan to that of the negative scan decreases with increase in T, Elevate the T reduces the poisoning effect
- ✓ E_{a,app} and A_{app} display a decline from 0.3 V to 0.5 V, mainly due to the potential induced changing of driving force.

$$k_{app}(E) = A_{app}(E) \cdot \exp\left(-\frac{E_{a,app}(E)}{RT}\right)$$

4. Conclusions

- ✓ WC nanoparticles supported Pd nanocatalysts (Pd/WC) were synthesized by ALD method and used for formic acid oxidation. Pd/WC possesses an electronic structure similar to that of pc-Pt.

- ✓ Pd/WC (SC5) exhibits FAO activity of ca. 3 mA/μg Pd @ 0.4 V vs RHE.

- ✓ Present study reveals that Pd/WC prepared by ALD method might serve to great potential to serve as good electrocatalysts for formic acid oxidation

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2. University of Science and Technology of China (USTC)
3. Chinese Academy of Science and The World Academy of Science (CAS TWAS)