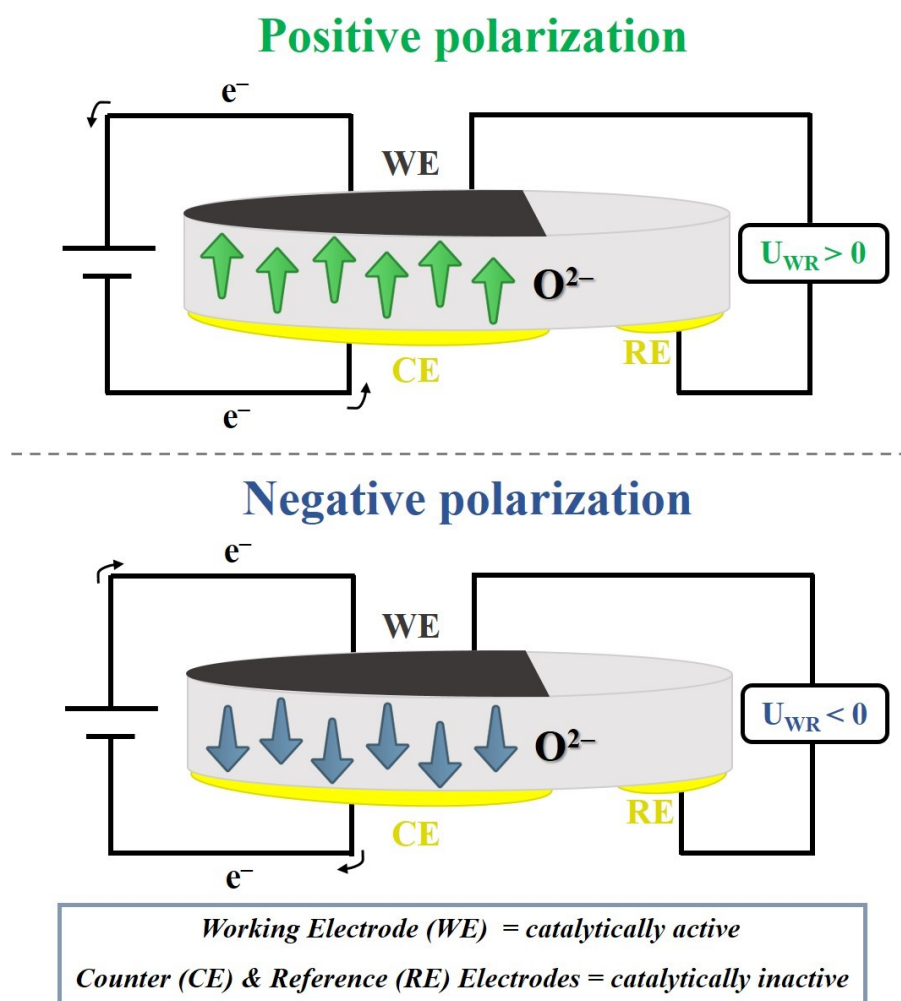


# Electrochemical control of the RWGS reaction over Ni nanoparticles deposited on yttria stabilized zirconia

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**Figure S1.** Principle and basic experimental setup for electrochemical promotion of catalysis (EPOC) experiments for an oxygen-ion conductor/solid electrolyte.

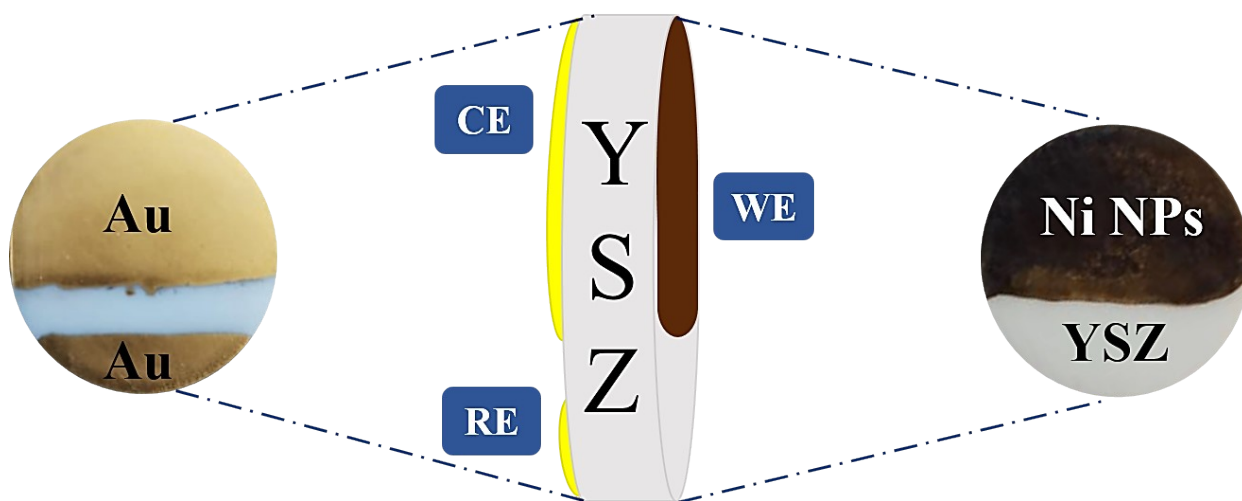


Figure S2. The fresh Ni/YSZ/Au sample.

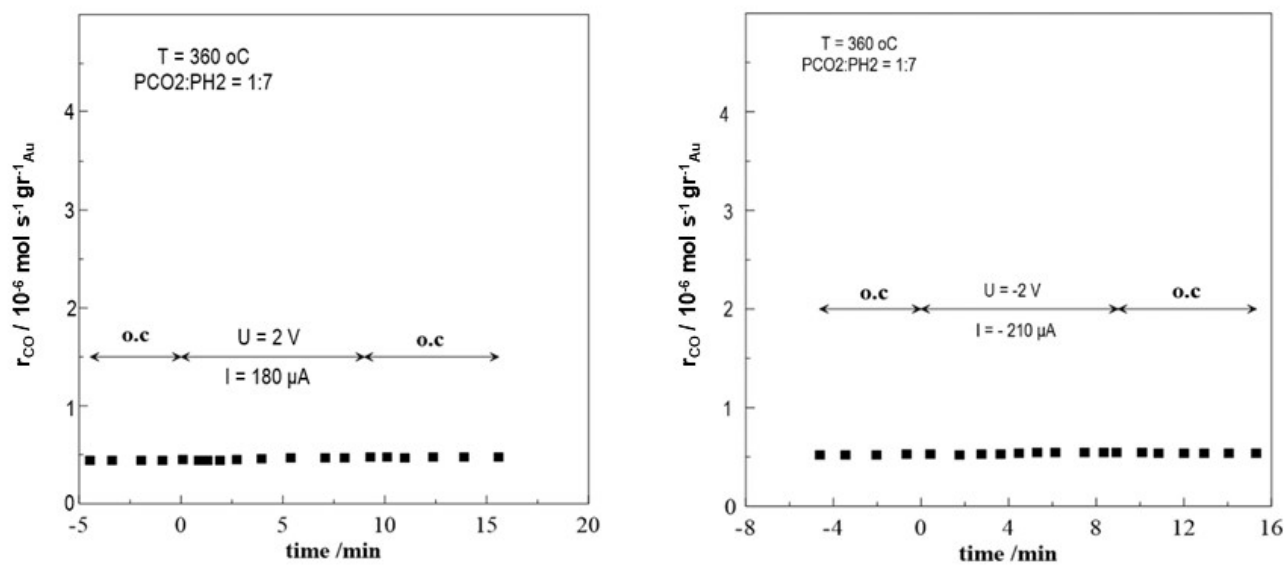
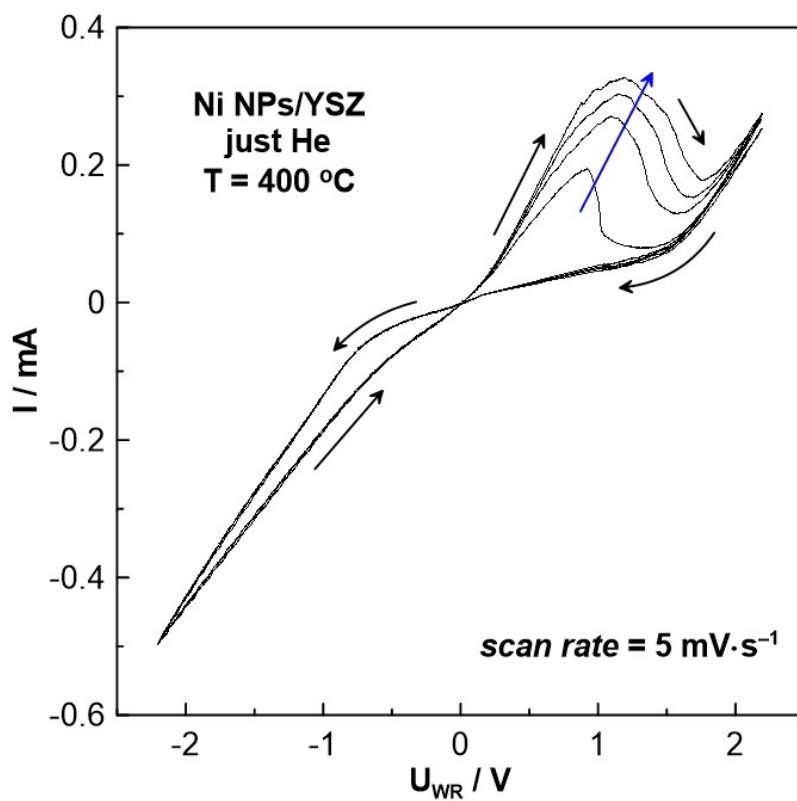
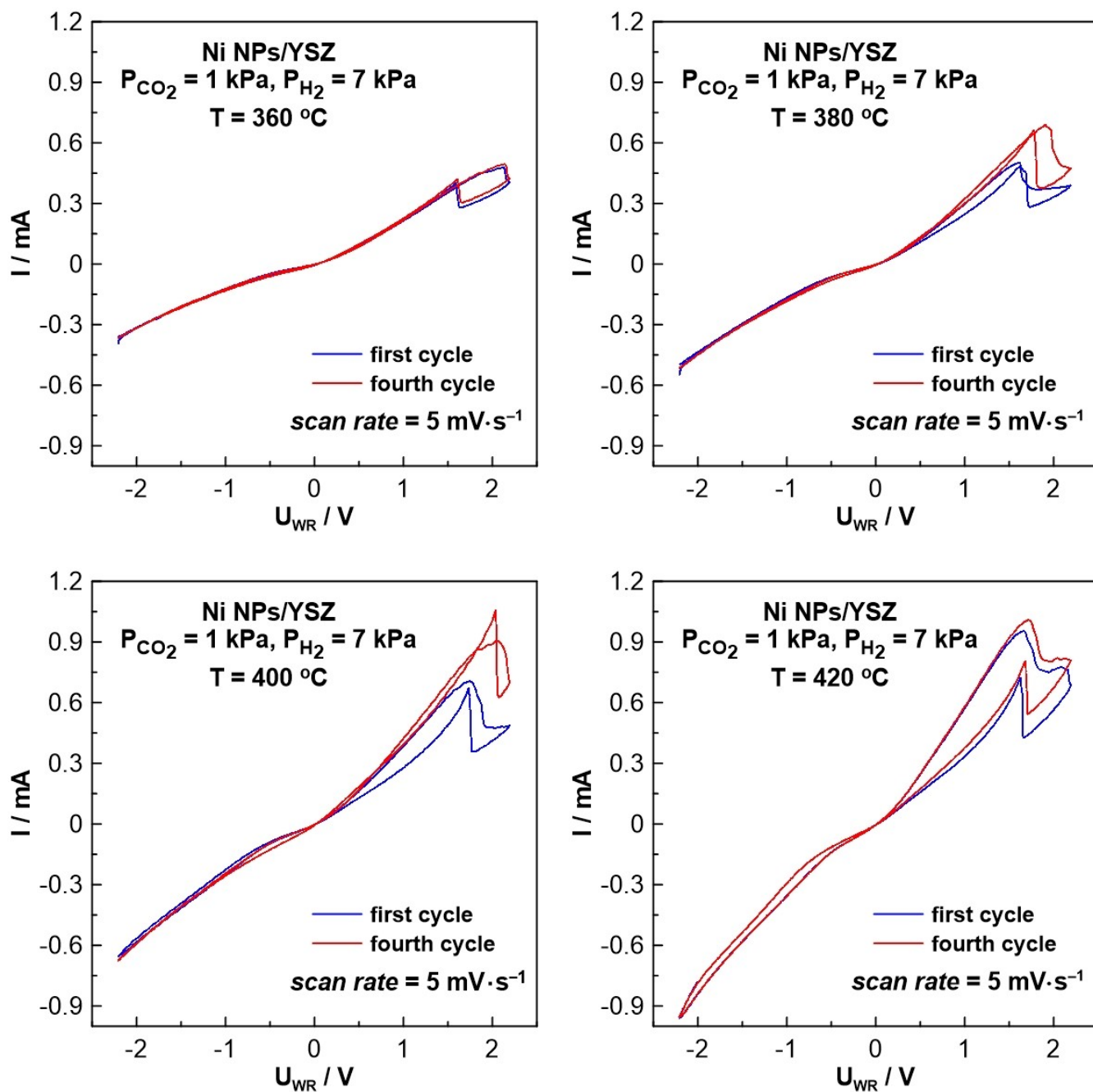


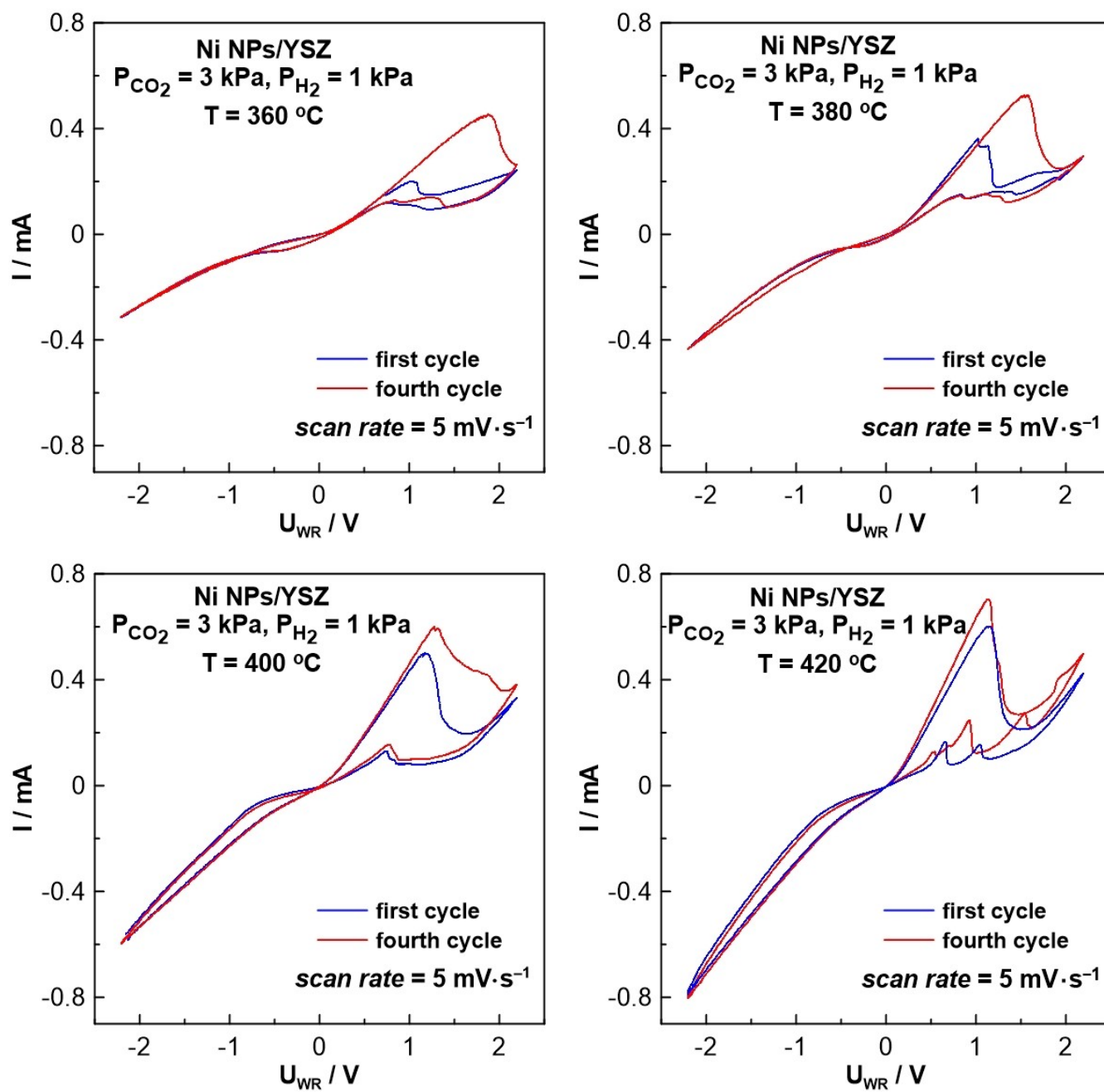
Figure S3. Transient effect of a constant (left) positive (+2 V) and (right) negative (-2 V) applied potential on the catalytic rate of CO formation over the Au/YSZ/Au sample (blank experiment).



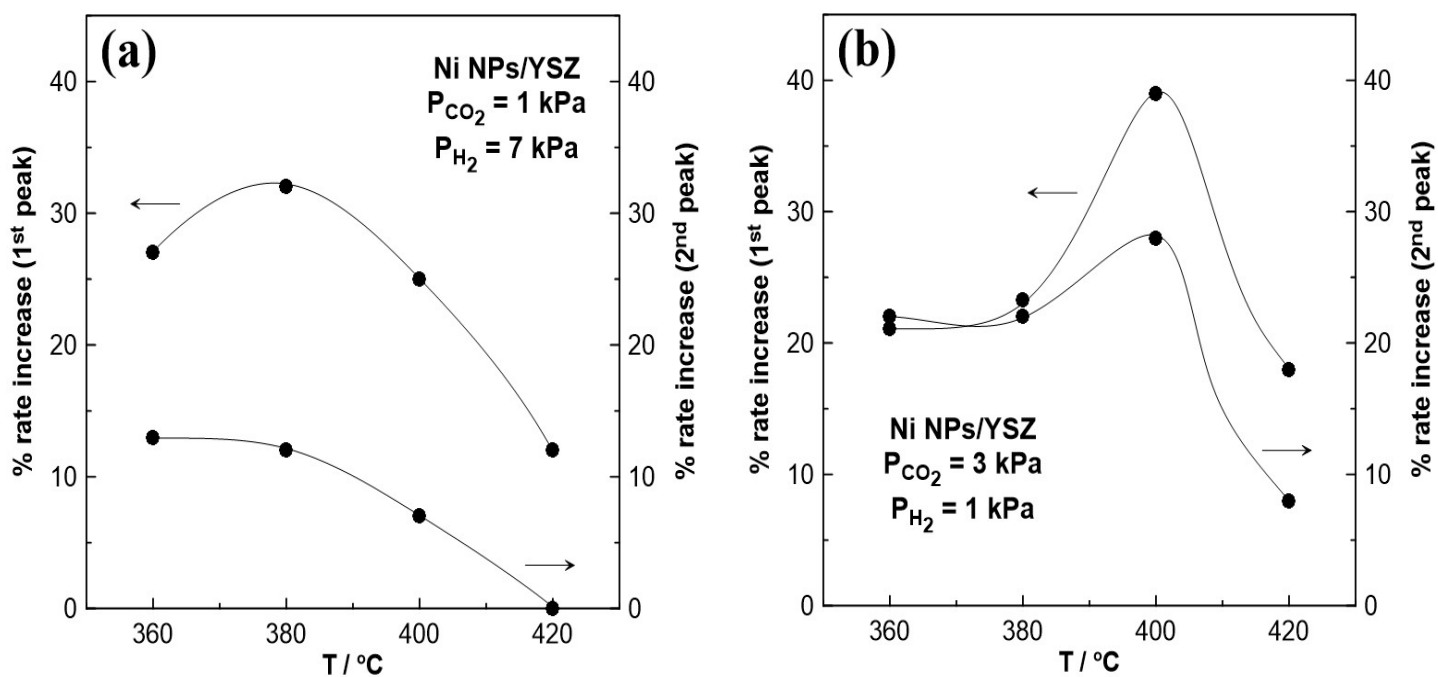
**Figure S4.** Cyclic voltammograms for the Ni NPs/YSZ sample under inert (i.e., He) atmosphere,  $T = 400\text{ °C}$ , scan rate =  $5\text{ mV}\cdot\text{s}^{-1}$ .



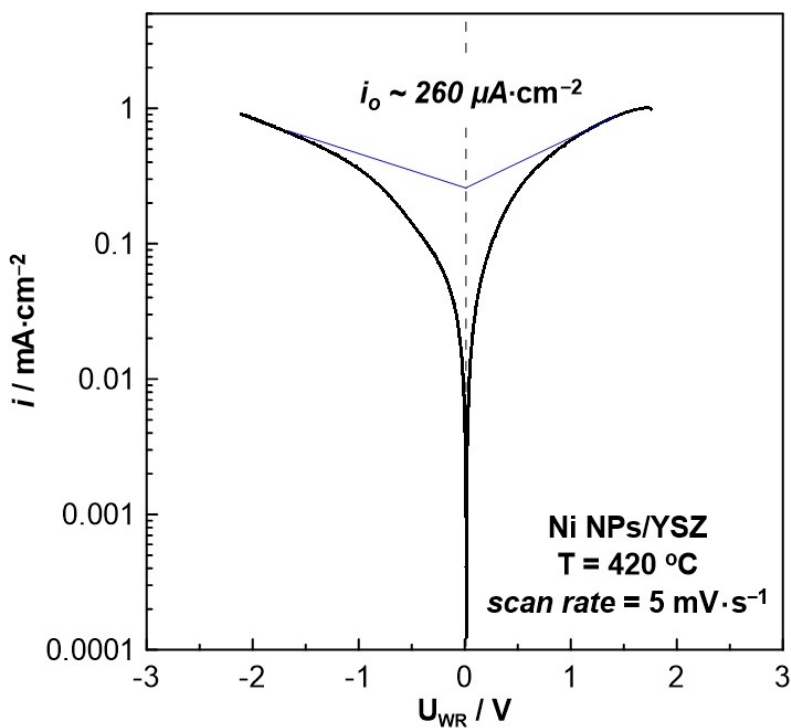
**Figure S5.** Effect of temperature on the shape of the cyclic voltammograms for Ni NPs on YSZ under reducing reaction conditions, scan rate = 5 mV·s<sup>-1</sup>.



**Figure S6.** Effect of temperature on the shape of the cyclic voltammograms for Ni NPs on YSZ under oxidizing reaction conditions, scan rate =  $5 \text{ mV} \cdot \text{s}^{-1}$ .



**Figure S7.** Effect of temperature on the % rate increase of the first- and second-rate peaks of CO formation upon positive (+2 V) polarization under: (a) reducing and (b) oxidizing reaction conditions.



**Figure S8.** Tafel plot for Ni NPs on YSZ at 420 °C under reducing ( $P_{\text{CO}_2} = 1 \text{ kPa}$ ,  $P_{\text{H}_2} = 7 \text{ kPa}$ ) conditions, scan rate = 5 mV·s<sup>-1</sup>.