

# Cerium titanate thin films: synthesis and characterization.

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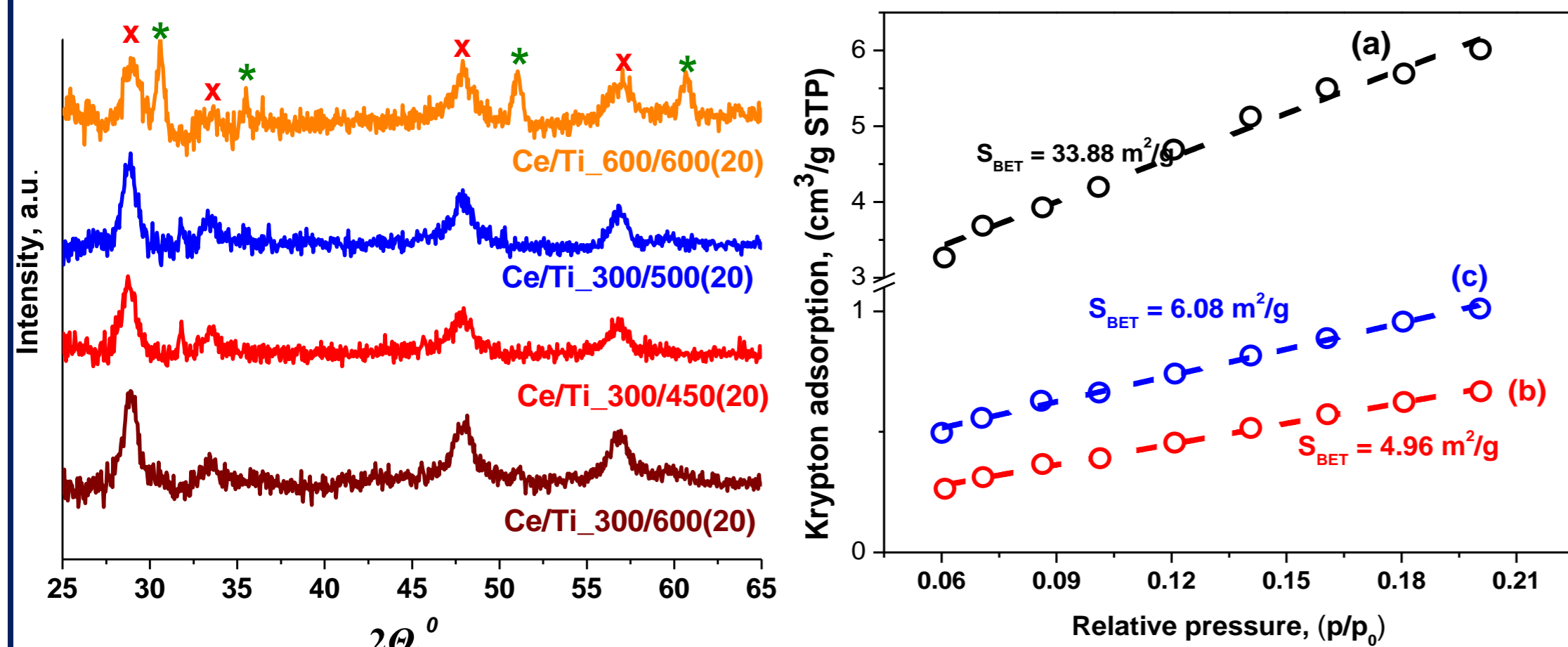
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Development of new semiconductive materials with unique physicochemical properties is important task of chemistry and physics. Metal titanates present the solid complex structures containing the common bonds between the metal ions ( $[-M-O-Ti-]$ ) that are responsible for the differed on bare metal oxides electronic and surface properties.

**Synthesis procedure.** The sol-gel method was used for the three layered  $Ce:Ti=1:1$  films creation using titanium(IV) isopropoxide,  $CeCl_3 \cdot 7H_2O$ , ethanol and perchloric acid. The formed sol was applied for the glass covering by dip-coating procedure. The different treatment temperatures of the films' layers as well as the calcination time were used to find out the optimal conditions for cerium titanate crystallization, as namely preliminary treatment of interlayered coatings at 300 °C or 500 °C or 600 °C and the final layer at 450 °C or 500 °C or 600 °C for 20 or 180 min (denoted as  $Ce/Ti\_X/Y(Z)$ , where X and Y are the temperatures of interlayered coating and final layer, respectively, and Z is duration of calcination in min).

## Structural and surface properties



Tab. 1. XRD patterns of  $Ce:Ti=1:1$  films treated at different temperatures:  $x-CeO_2, *-Ce_2Ti_2O_7$

Fig. 2. BET specific surface area plot for  $Ce/Ti_{300/450(20)}$  (a),  $Ce/Ti_{600/600(20)}$  (b) and  $TiO_{2\_300/450(20)}$  (c).

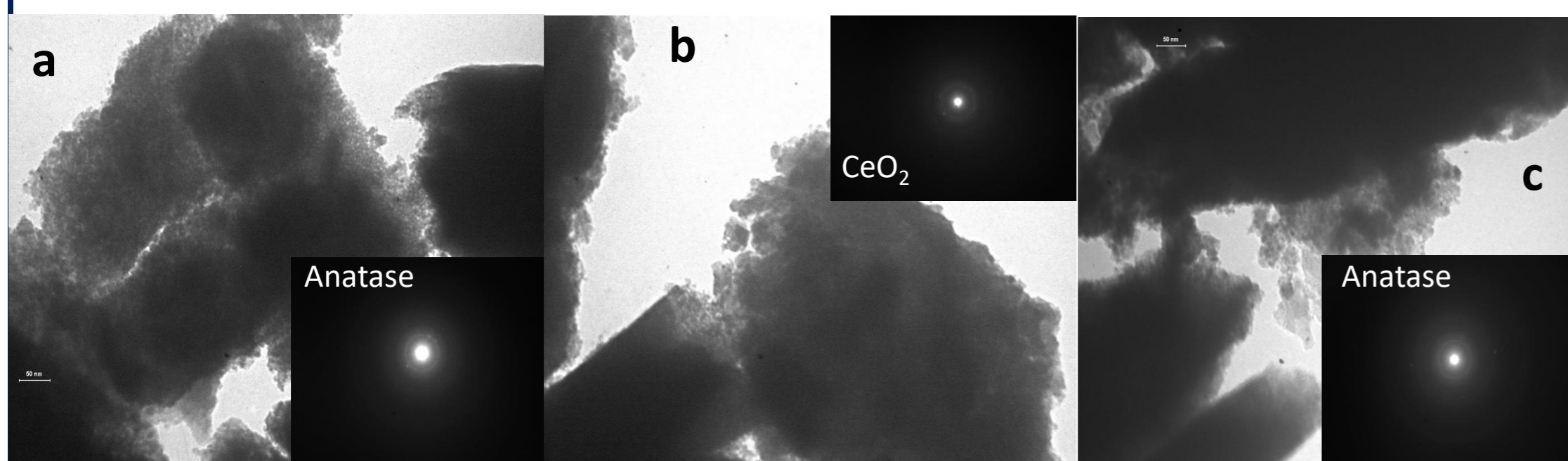


Fig. 3. TEM and electron diffraction images of  $Ce/Ti_{300/450(20)}$  (a, b) and  $Ce/Ti_{600/600(20)}$  (c) films.

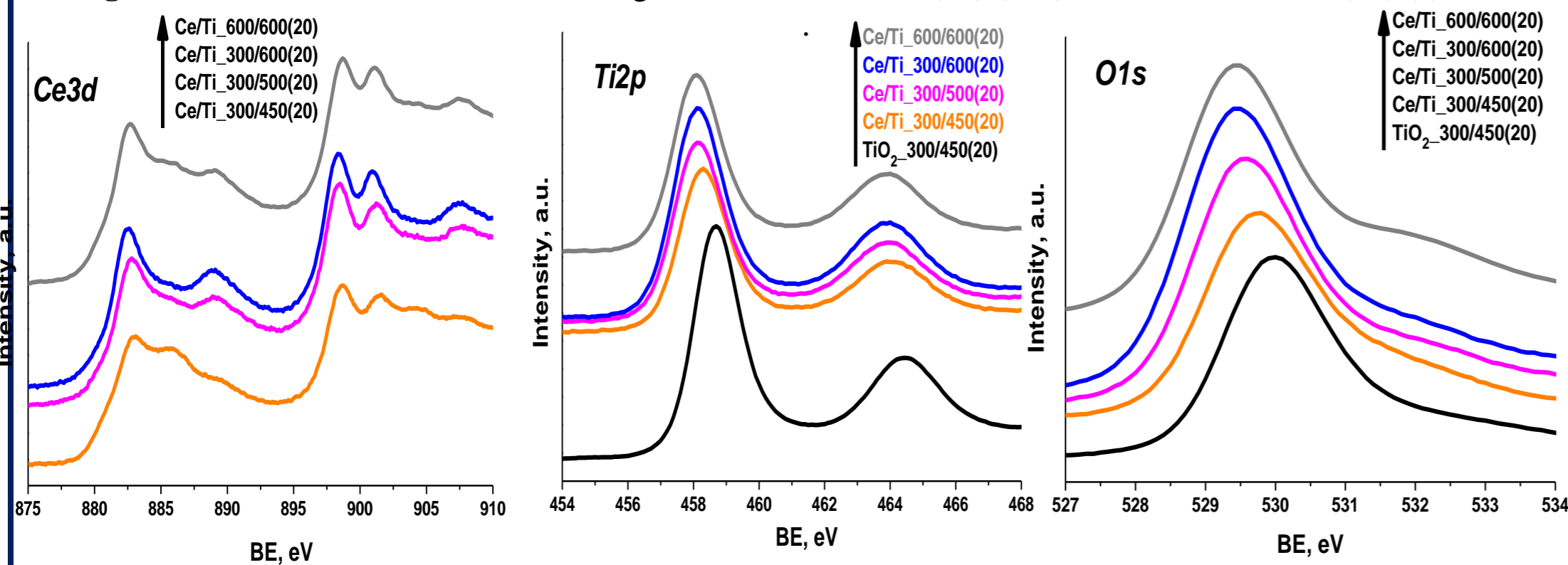


Fig. 4.  $Ce3d$ ,  $Ti2p$  and  $O1s$  XPS spectra of the films.

Film	At., %			Ratio		
	Ce	Ti	O	Ce : Ti : O	$M^* : O$	$Ce^{3+} : Ce^{4+}$
$Ce/Ti_{300/450(20)}$	7.6	26.3	66.1	1.0:3.4:8.6	1.0 : 1.9	1.0 : 2.6
$Ce/Ti_{300/500(20)}$	6.9	25.4	67.7	1.0:3.7:9.8	1.0 : 2.1	1.0 : 5.3
$Ce/Ti_{300/600(20)}$	6.5	25.6	67.9	1.0:3.9:10.5	1.0 : 2.1	1.0 : 6.5
$Ce/Ti_{600/600(20)}$	7.6	21.7	70.7	1.0:2.8:9.2	1.0 : 2.4	1.0 : 2.2

Tab. 1. Atomic content and ratios of elements and ions for the films obtained from XPS data

It is shown that the preliminary treatment of interlayered coatings at 300 °C leads to crystallization of  $CeO_2$  (10-15 nm) and anatase (2-6 nm), whereas  $CeO_2$  (10-15 nm),  $Ce_2Ti_2O_7$  (16-21 nm) and anatase (4-9 nm) are formed at 600 °C. BET surface area data confirm non-porous structure of the surface and show that the chemical composition and treatment procedure influence on the adsorption capability of the samples. The XPS data indicate that the films' surface contains in 3-4 times higher atomic content of Ti than Ce one in the case of the films with interlayered coatings at 300 °C while more Ce ions are present on the surface of  $Ce/Ti_{600/600(20)}$  film. The  $Ce^{3+}$  and  $Ce^{4+}$  ions are detected for all the films. The highest content of  $Ce^{3+}$  ions is fixed for the film with interlayered coating at 600 °C. The chemical shift of  $Ti2p$  and  $O1s$  XPS maxima is suggested to be connected to Ce-O-Ti bonds, as namely cerium titanate phase formation

## Photoelectrochemical investigation

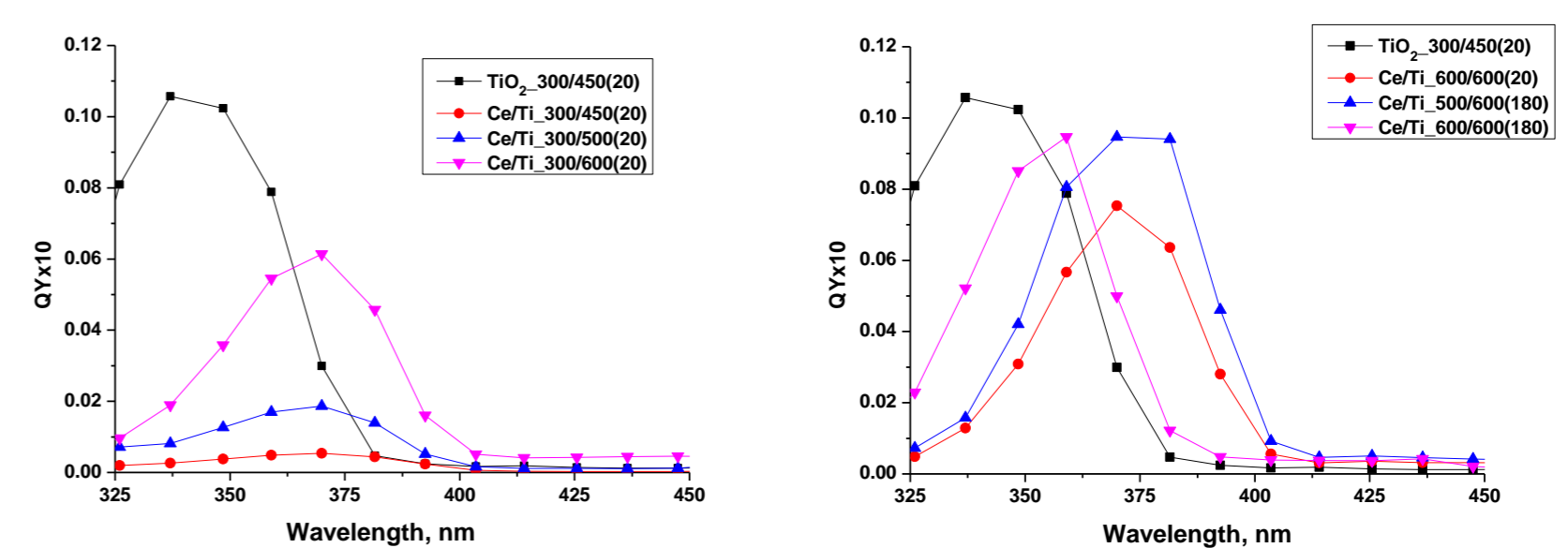


Fig. 1. Quantum yield of photocurrent vs wavelength for  $Ce:Ti=1:1$  films.

Film	$E_{BG}$ , eV	$E_{fb}$ , V	$E_{VB}$ , V
$TiO_{2\_300/450(20)}$	3.2	-0.4	+2.8
$Ce/Ti_{300/450(20)}$	2.9	-0.8	+2.1
$Ce/Ti_{300/500(20)}$	2.9	-0.7	+2.2
$Ce/Ti_{300/600(20)}$	3.0	-0.6	+2.4
$Ce/Ti_{600/600(20)}$	3.0	-0.8	+2.2
$Ce/Ti_{600/600(180)}$	3.0	-0.9	+2.1
$Ce/Ti_{500/600(180)}$	3.0	-1.0	+2.0

Tab. 1. Bandgap energy, flat band potentials and energy of the valence band of  $Ce:Ti=1:1$  films.

The maximum of photocurrent quantum yield (QY) is shifted to longer wavelength for all  $Ce:Ti=1:1$  films compared to  $TiO_2$  one. The bandgap of these films is also narrowed to 2.9 and 3.0 eV. The flat band potential ( $E_{fb}$ ) is cathodically shifted for all  $Ce:Ti=1:1$  films whereas the energy of the valence band becomes to be less positive compared to  $TiO_2$  one.

## Electrocatalytic activity in $H_2$ evolution reaction

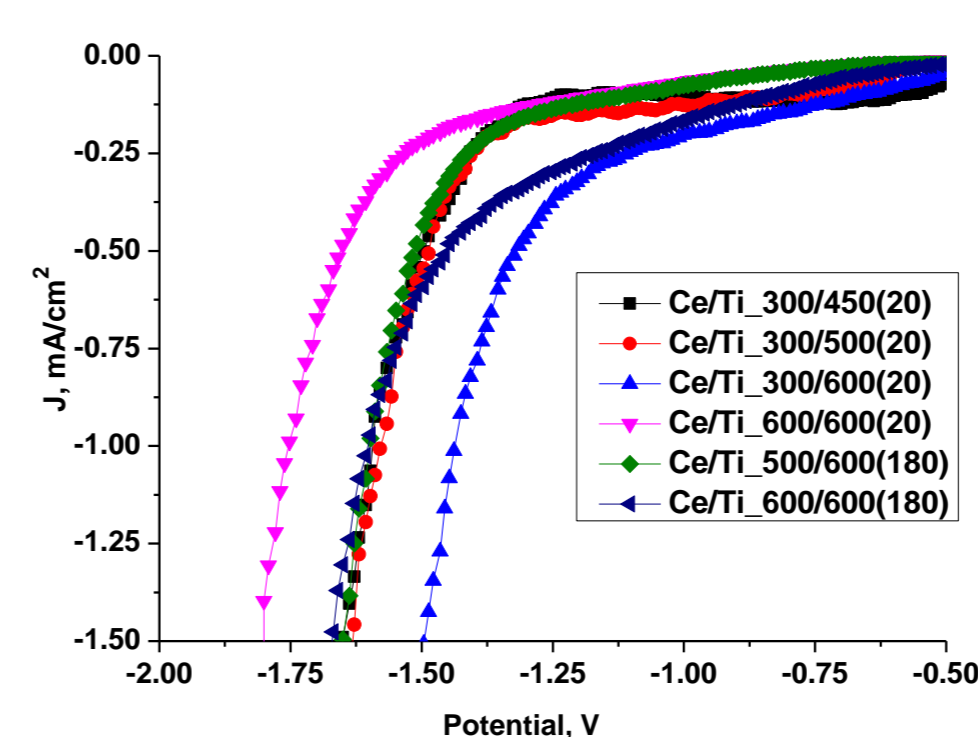


Fig. 3. Polarization curves of the electrodes vs. Ag/AgCl electrode

The electrocatalytic hydrogen evolution reaction occurs over all  $Ce:Ti=1:1$  electrodes at the potentials from -1.2 V to -1.8 V.

The efficiency of this reaction over the samples is:  
 $Ce/Ti_{300/600(20)} >$   
 $Ce/Ti_{300/500(20)} \approx$   
 $Ce/Ti_{300/450(20)} >$   
 $Ce/Ti_{500/600(180)} >$   
 $Ce/Ti_{600/600(180)} >$   
 $Ce/Ti_{600/600(20)}$

## CONCLUSIONS

It is shown that variation of calcination temperature of sol-gel coating layers and its duration affect on the structural composition of the films. The presence of Ce ions retards the crystallization of  $TiO_2$  even at 600 °C. The crystalline phases of  $CeO_2$ ,  $Ce_2Ti_2O_7$  and  $TiO_2$  are detected at the calcination of layers at 600 °C. Photoelectrochemical results reveal that  $Ce/Ti$  films are characterized by the shift of maximum of photocurrent quantum yield to lower wavelength, the lower band gap energy and more negative flat band and valence band potentials compared to  $TiO_2$ . Based on XPS results, it is suggested that  $Ce^{4+}$  ions are influenced on the electrocatalytic hydrogen evolution reaction rather than Ce-O-Ti bonds.