

ENHANCED STABILITY AND ELECTROCHEMICAL PERFORMANCE OF A BaTiO₃/PbO₂ ELECTRODE VIA A LAYER OBTAINED WITH LAYER ELECTRODEPOSITION

IZBOLJŠANA STABILNOST IN ELEKTROKEMIJSKA ZMOGLJIVOST ELEKTRODE BaTiO₃/PbO₂, IZDELANE Z ELEKTRODEPOZICIJO PLAST NA PLAST

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Herein, the electrodeposition of BaTiO₃ and PbO₂ on Ti using the layer-by-layer method under different current densities (*CDs*) and times, was investigated. The weight difference in the deposited BaTiO₃ explains the BaTiO₃ weight decrease by one order with the increasing *CD* from 0.025 A cm⁻² to 0.125 A cm⁻² and also follows the same trend during the PbO₂ deposition. The PbO₂ deposition at different *CDs* demonstrates that the deposited PbO₂ weight increases by one order with the increasing *CD*. Also, cyclic voltammetry results explain the low and moderate deposition *CDs* and the time suitably shows the PbO₂ redox behavior. According to SEM and XRD, a *CD* of 0.05 A cm⁻² affects the formation of crystalline BaTiO₃ and PbO₂ more than higher or lower *CDs*. Finally, the BaTiO₃ and PbO₂ layer-by-layer electrode electrodeposited at a moderate *CD* showed a better stability than the electrode including only PbO₂. The use of BaTiO₃ is promising for the stability of the PbO₂ electrode preparation.

Keywords: BaTiO₃, PbO₂, electrodeposition, layer by layer, electrode stability

Preiskovana je bila elektrodepozicija BaTiO₃ in PbO₂ na Ti, z uporabo metode plast na plast, pri različnih časih in gostotah toka (*CD*). Razlike v teži BaTiO₃ razložijo naraščanje teže BaTiO₃ za red velikosti zaradi naraščanja *CD*, od 0,025 A cm⁻² do 0,125 A cm⁻². Podoben trend je bil opažen tudi pri nanašanju PbO₂. Pri nanašanju PbO₂, različni *CD* kažejo naraščanje teže nanosenega PbO₂ za red velikosti z naraščanjem *CD*. Tudi ciklična voltometrija razloži majhen in srednji *CD* in čas ustrezno kaže redoks vedenje PbO₂. SEM in XRD z 0,05 A cm⁻² vodita nastanek kristaliničnega BaTiO₃ in PbO₂ bolj kot višji in nižji *CD*. Končno se kaže boljša stabilnost elektrode elektronanešenega BaTiO₃ in PbO₂ plast na plast pri zmernih *CD*, kot pa pri PbO₂ elektrodi. Uporaba BaTiO₃ je obetajoča za stabilnost priprave PbO₂ elektrode.

Ključne besede: BaTiO₃, PbO₂, elektro nanašanje, plast na plast, stabilnost elektrode

1 INTRODUCTION

PbO₂ clearly emerges as an attractive material used as an anode for a direct oxidation of organic compounds due to its high oxygen-evolution potential, low price, relative stability under the high positive potentials required, stability at high temperatures and ease of preparation.¹⁻³ Its high overpotential for O₂ evolution allows the application of potentials to about 2.0 V versus a saturated calomel electrode (SCE) in an acidic medium without vigorous O₂ evolution.⁴ The PbO₂ electrodes have some disadvantages, i.e., they corrode at high rates under reducing conditions and in some acids, and they have poor mechanical properties. Its composites with various oxides (e.g., Al₂O₃, RuO₂, and TiO₂) are known⁴⁻⁶ for a high catalytic activity and stability. Among many ways of preparation, such as the sol-gel technology, the plasma-chemical method, etc., the electrochemical synthesis is the most promising method, easy to implement, allowing the technological parameters to be varied smoothly for a better control of the

composition and properties of the resulting composites.⁴⁻⁶

The α - and β -types of PbO₂, applied layer by layer on metal anodes have been widely used in electrolysis.^{7,8} Generally, titanium is not a viable substrate for practical electrodes in electrodepositing non-ferrous metals. Aluminum is relatively cheap and has a good conductivity. The electrode material obtained by electrodepositing lead dioxide on an Al substrate has huge market prospects. A stress-free intermediate α -PbO₂ coating is produced with electrodeposition from an alkaline lead bath⁹ and it plays the role of the binder on the top α -PbO₂ coating, improving the service life of the electrode. A non-conducting ceramic material has also been used as the substrate to achieve a high stability of PbO₂ with the fluorine resin as the co-dopant on the upper layer.¹⁰

In the present investigation, perovskite-type BaTiO₃ is applied to Ti as the lower layer using the hydrothermal electrodeposition method. As the top/upper layer, PbO₂ is to be applied. The effects of the thickness of both layers are controlled with the current density and the deposition

time to achieve the electrode stability and activity. Thus, the main work of this paper deals with the layer-by-layer deposition of BaTiO₃ and PbO₂ and its influence on the PbO₂ electrode stability and electrochemical application as a sandwich-type electrode.

2 EXPERIMENTAL DETAILS

2.1 Electrodeposition

Electrolysis was performed using a DC power supply, BS 32C (0–100 V, 0–50 A) from the Korea Switching Company, Korea, using the constant-current mode (the galvanostatic mode). Before the electrolysis start, the anode was initially immersed in the electrolyte for 1 min to stabilize its surface state. The deposition was performed in two steps: in the first step, BaTiO₃ was formed as the lower coating on a pretreated Ti electrode at 65 °C using a current-density range of 0.025–0.125 A cm⁻² for 15–60 min. The BaTiO₃ deposited electrode was washed after its deposition in hot ammonia water adjusted to pH 11 to minimize the BaCO₃ formation. It was then rinsed in purified Millipore water and cleaned in ethanol with an ultrasonic cleaner for 1 min. Then, β-PbO₂ was deposited as the upper layer using a current-density (*CD*) range of 0.025–0.125 A cm⁻² for 15–60 min in a 0.1 M HNO₃ medium at 65 °C.

2.2 Analysis

Cyclic-voltammetry (CV) measurements were performed using a VersaSTAT3 from Princeton Applied Research, USA. The electrochemical cell was a three-electrode cell with a working electrode, a platinum-plate counter electrode and an Ag/AgCl reference electrode. The working electrode was prepared with the electrodeposition method. Scanning electron microscopy of the prepared PbO₂ electrodes was carried out with Zeiss EVO MA10 to investigate the surface morphology of the films. The XRD patterns of the as-prepared PbO₂ samples were obtained from an X'PERT-PRO X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.1540598$ nm). The electrolysis was done using a DC power supply from KSC, Korea, with an applied *CD* of 0.3 A cm⁻² in 1 M H₂SO₄.

3 RESULTS AND DISCUSSIONS

3.1 Selection of deposition conditions

As the *CD* and time are the key factors to control the deposition, the initial work was done to identify the suitable deposition time and *CD* for the first and second layers of BaTiO₃ and PbO₂, respectively. First, the BaTiO₃ layer was deposited using four different *CD*s of (0.025, 0.05, 0.1, 0.125) A cm⁻² with four different durations such as (15, 30, 45, 60) min, by keeping the PbO₂ (the second layer) deposition parameters (*CD* = 0.05 A cm⁻², 30 min duration) constant. As mentioned in

the experimental section, the BaTiO₃ and PbO₂ depositions were done in different solutions and the obtained results are tabulated in **Table 1**. It is seen from the 1st row and 4th column of **Table 1** that the weight of the deposited BaTiO₃ shows no consistency with different deposition times (15–60 min) within a single *CD* (0.025 A cm⁻²); a similar inconsistency is also shown for the PbO₂ deposition, the 5th column. However, with the increasing *CD* during the BaTiO₃ deposition from 0.025 to 0.125 A cm⁻², shown in the 1st to the 4th rows, the deposited BaTiO₃ weight is reduced by one order from 0.01 to 0.001 (the 5th column).

Table 1: Deposited-electrode weight difference in each step of: 1) BaTiO₃ and 2) PbO₂ at different current densities and times

Tabela 1: Razlika v masi nanešene elektrode za vsako stopnjo: 1) BaTiO₃ in 2) PbO₂ pri različnih gostotah tokov in časih

BaTiO ₃ coating		PbO ₂ coating		Electrode weight difference (g)	
<i>CD</i> [@] (A cm ⁻²)	Time (min)	<i>CD</i> [@] (A cm ⁻²)	Time (min)	BaTiO ₃	PbO ₂
0.025	15	0.05	30	0.0222	0.2837
	30		0.0181	0.2929	
	45		-0.0034	0.3043	
	60		0.024	0.3041	
0.05	15	0.05	30	-0.0027	0.0649
	30		0.0052	0.2681	
	45		0.0055	0.2969	
	60		-0.0087	0.2997	
0.1	15	0.05	30	0.0094	0.0908
	30		0.0054	0.0217	
	45		-0.0089	0.0338	
	60		-0.0076	0.0800	
0.125	15	0.05	30	0.0032	0.0702
	30		-0.0372	*	
	45		0.0629	*	
	60		0.0397	0.0456	
0.025	30	0.025	15	0.0159	-0.0318
			30	0.0091	-0.0133
			45	0.0084	0.1065
			60	0.0167	0.4092
0.025	30	0.05	15	-0.0594	0.2779
			30	0.0105	0.2188
			45	-0.0180	0.0140
			60	-0.0065	0.5551
0.025	30	0.1	15	0.1020	0.1611
			30	-0.0423	0.3547
			45	-0.0137	0.4100
			60	-0.0362	0.2384
0.025	30	0.125	15	*	*
			30	*	*
			45	*	*
			60	*	*

*Dissolution of electrode, [@]*CD* = current density, lower than the original weight

In a similar way, the deposited PbO₂ weight also decreases by one order with the increasing *CD* (the 6th column – from 0.1 to 0.01). At the same time, the results are different if the PbO₂ deposition *CD* is varied at a

fixed CD and time of the BaTiO₃ deposition (5th to 8th rows of **Table 1**) where the weight of BaTiO₃ is maintained constant but the deposited PbO₂ weight is increased by one order with the increasing CD (the 6th column of the 5th to 8th rows in **Table 1**). It is maintained on the basis of the results that the formation of BaTiO₃ on the Ti electrode influenced further deposition of PbO₂, which means that the conductivity was lower when BaTiO₃ completely covered the electrode due to the dielectric properties of BaTiO₃. A similar trend applied to the PbO₂ deposition carried out at a high CD and a fixed, low CD of the BaTiO₃ deposition where a complete dissolution of the deposited film was observed.

Further, through a CV analysis, the electron-transfer behavior of the deposited electrode can be inferred on the basis of PbO₂ redox properties. **Figure 1a** shows the PbO₂ redox response to the effects of various CD s and

times of the BaTiO₃ deposition, where no redox peaks for PbO₂ are observed except for two CD variations in the BaTiO₃ deposition: 0.025 (45 min) A cm⁻² and 0.05 (45 min) A cm⁻². In all the remaining conditions, only a charge transfer like the CV response is observed. In the case of the variation in the PbO₂ deposition, 60 min and 0.025 A cm⁻² or 0.05 A cm⁻², CD only shows redox peaks that resemble PbO₂,¹¹ as shown in **Figure 1b**. Under another two conditions, a CD of 0.1 A cm⁻² over 45 min and 60 min deposition times, the PbO₂ deposition indicates a low oxidation current. All the remaining conditions show a charging current like the CV response without any redox peaks as not enough PbO₂ is exposed on the electrode surface. This is well correlated with the deposited weight of PbO₂ in the 1st, 2nd and 7th rows of the 6th column of **Table 1**, where only the deposited PbO₂ weight is higher than in the other conditions.

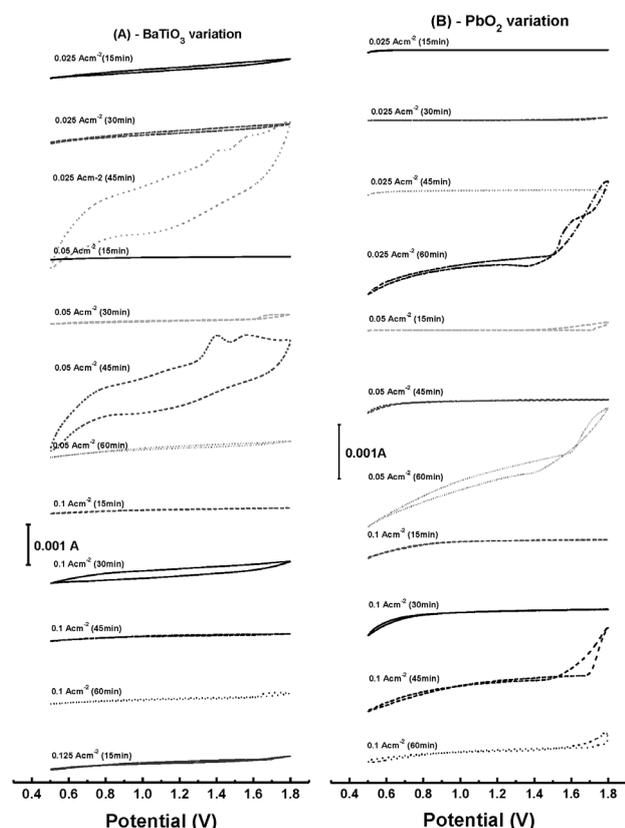


Figure 1: CV results for electrodeposited BaTiO₃/PbO₂ using different current densities and times in a 0.1 M phosphate buffer solution at a scan rate of 20 mV s⁻¹: a) variation in BaTiO₃ deposition current density and time with fixed current density and time (0.05 A cm⁻², 30 min) of PbO₂ deposition, b) variation in PbO₂ deposition current density and time with fixed current density and time (0.025 A cm⁻², 30 min) of BaTiO₃ deposition

Slika 1: Rezultati ciklične voltmetrije elektro nanešenega BaTiO₃/PbO₂, pri uporabi različnih gostot tokov in časov, v 0,1 M fosfatni puferski raztopini pri hitrosti skeniranja 20 mV s⁻¹: a) spreminjanje gostote toka in časa nanašanja BaTiO₃ od stalne gostote toka in časa (0,05 A cm⁻², 30 min) pri nanašanju PbO₂, b) spreminjanje gostote toka in časa nanašanja PbO₂ pri stalni gostoti toka in časa (0,025 A cm⁻², 30 min) nanašanja BaTiO₃

3.2 Morphological characterization

SEM images of the BaTiO₃ and PbO₂ deposited at different conditions are depicted in **Figure 2**. The first layer of BaTiO₃ shows no distinctive difference in the SEM image and it looks almost like a needle structure in micrometer size, as shown in **Figure 2a**. Both layers deposited at 0.025 A cm⁻² show a densely deposited PbO₂ layer (**Figure 2b**). There is a defect in the PbO₂

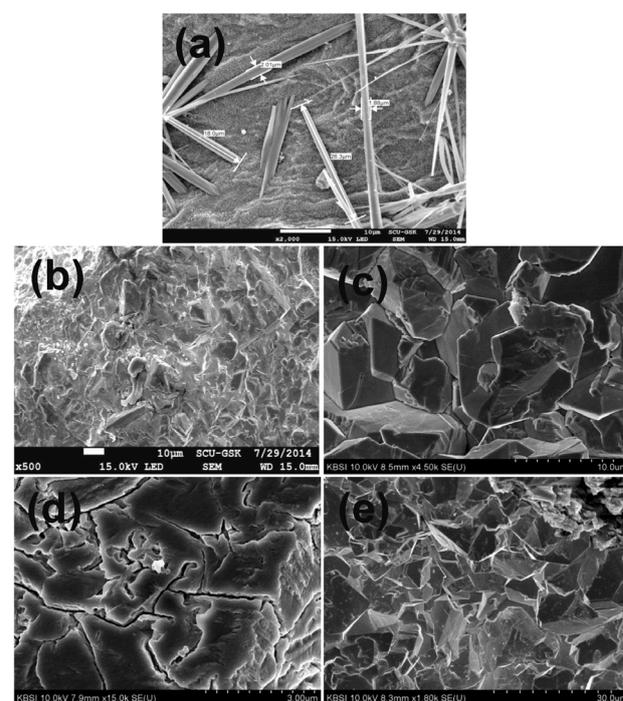


Figure 2: SEM images of BaTiO₃ and PbO₂ electrodes, deposited at different CD s and times: a) BaTiO₃^{0.1(45 min)}, b) BaTiO₃^{0.025(30 min)/PbO₂^{0.025(60 min)}, c) BaTiO₃^{0.025(30 min)/PbO₂^{0.1(60 min)}, d) BaTiO₃^{0.05(45 min)/PbO₂^{0.05(30 min)}, e) BaTiO₃^{0.1(45 min)/PbO₂^{0.05(30 min)}}}}}

Slika 2: SEM-posnetki BaTiO₃ in PbO₂ elektrod, nanešenih pri različnih CD in časih: a) BaTiO₃^{0.1(45 min)}, b) BaTiO₃^{0.025(30 min)/PbO₂^{0.025(60 min)}, c) BaTiO₃^{0.025(30 min)/PbO₂^{0.1(60 min)}, d) BaTiO₃^{0.05(45 min)/PbO₂^{0.05(30 min)}, e) BaTiO₃^{0.1(45 min)/PbO₂^{0.05(30 min)}}}}}

coating if the PbO₂ deposition *CD* increased to 0.1 A cm⁻² (Figure 2c). The film cracking is more dominant if both layers were deposited at a *CD* of 0.05 A cm⁻² (Figure 2d). The film cracking is more enhanced if the BaTiO₃ layer was deposited at 0.1 A cm⁻² (Figure 2e). When both layers were deposited at a low *CD* of 0.025 A cm⁻², there is a smooth layer with smaller particles.

Figure 3a shows the XRD patterns of the BaTiO₃ deposited electrodes using different *CD*s and times with a fixed PbO₂ deposition. With the applied *CD* of 0.05 A cm⁻², the BaTiO₃ peak reflections are less intense at 2θ values of about 31.03, 38.58, 41.88, and 55.47 (VRC# 01-075-0213) along with the Ti reflections. Additionally, BaCO₃ also appeared on the surface, with a 2θ peak at about 23.85 (VRC# 00-044-1487) that might have occurred after the deposition of BaTiO₃ due to high pH.¹² The BaTiO₃ peak intensity increased when the deposition *CD* increased to 0.1 A cm⁻² as shown on curve b in Figure 3a. The lowest *CD* (0.025 A cm⁻²) caused a decrease in the crystallinity of BaTiO₃, which turned to the amorphous phase; see a broad peak between 2θ of

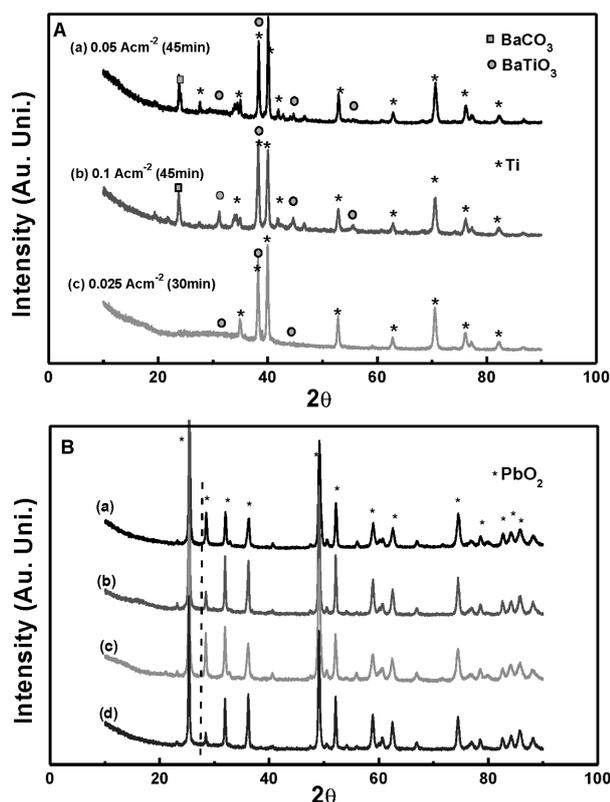


Figure 3: a) XRD patterns of current-density and time variation (mentioned in the figure) of BaTiO₃ deposition, b) XRD patterns of BaTiO₃/PbO₂ prepared at various current densities and times: a) BaTiO₃^{0.025(30 min)}/PbO₂^{0.025(60 min)}, b) BaTiO₃^{0.025(30 min)}/PbO₂^{0.1(60 min)}, c) BaTiO₃^{0.05(45 min)}/PbO₂^{0.05(30 min)}, d) BaTiO₃^{0.1(45 min)}/PbO₂^{0.05(30 min)}

Slika 3: a) Rentgenogram spreminjanja gostote toka in časa pri nanašanju BaTiO₃, b) rentgenogram BaTiO₃/PbO₂ pripravljene pri različnih gostotah toka in časih: a) BaTiO₃^{0.025(30 min)}/PbO₂^{0.025(60 min)}, b) BaTiO₃^{0.025(30 min)}/PbO₂^{0.1(60 min)}, c) BaTiO₃^{0.05(45 min)}/PbO₂^{0.05(30 min)}, d) BaTiO₃^{0.1(45 min)}/PbO₂^{0.05(30 min)}

20–35 on curve c of Figure 3. In the case of the PbO₂ deposition, the deposited electrode using various *CD*s and times shows peaks for the PbO₂ formation (VRC# 01-076-0564) as shown in Figure 3b. The only difference found is a peak-intensity decrease at a 2θ value of about 28.49 when the PbO₂ is deposited at 0.1 A cm⁻² and 0.05 A cm⁻² (60 min and 30 min) on the top of the BaTiO₃ deposition using the 0.025 A cm⁻² and 0.1 A cm⁻² *CD*s in the 30 min and 45 min durations (Figure 3b, curves b and d).

It is evident from the results that the 2θ of 28.49 belongs to the $\alpha(111)$ plane¹³, whose peak intensity is reduced, which means that the β -PbO₂ formation is predominant at this given condition. As seen on curve b in Figure 3a, the BaTiO₃ formation is more prominent at the 0.05 A cm⁻² *CD*, which means that the BaTiO₃ concentration increases the β -PbO₂ formation during the PbO₂ deposition. It is well known that the β -PbO₂ formation enhances the catalytic activity tremendously.¹⁴

3.3 Stability analysis

In order to apply the prepared electrodes, the selectively prepared electrodes obtained their stability in 1 M H₂SO₄ due to an enhanced *CD* of 0.3 A cm⁻², as depicted in Figure 4. An electrode that was prepared at a *CD* of 0.05 A cm⁻² (45 min) for BaTiO₃ and at 0.05 A cm⁻² (30 min) for the PbO₂ deposition showed a 3.9 V cell voltage up to 110 h (Figure 4, curve a); and after the potential sharply increased to 22 V the prepared electrode was decomposed. In the case of the increase in the BaTiO₃ deposition at the *CD* of 0.1 A cm⁻² when the

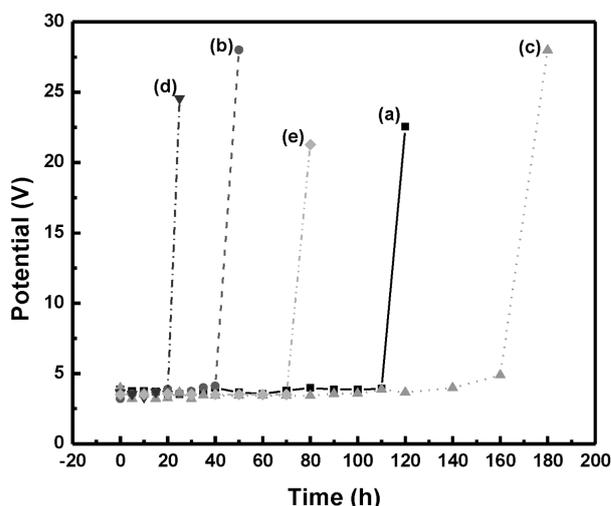


Figure 4: Electrolysis of different electrodes in 1 M H₂SO₄ at accelerated current density of 0.3 A cm⁻²: a) BaTiO₃^{0.05(45 min)}/PbO₂^{0.05(30 min)}, b) BaTiO₃^{0.1(45 min)}/PbO₂^{0.05(30 min)}, c) BaTiO₃^{0.025(30 min)}/PbO₂^{0.025(60 min)}, d) BaTiO₃^{0.025(30 min)}/PbO₂^{0.1(60 min)}, e) PbO₂^{0.025(60 min)}

Slika 4: Elektroliza različnih elektrod v 1 M H₂SO₄ pri pospešeni gostoti toka 0,3 A cm⁻²: a) BaTiO₃^{0.05(45 min)}/PbO₂^{0.05(30 min)}, b) BaTiO₃^{0.1(45 min)}/PbO₂^{0.05(30 min)}, c) BaTiO₃^{0.025(30 min)}/PbO₂^{0.025(60 min)}, d) BaTiO₃^{0.025(30 min)}/PbO₂^{0.1(60 min)}, e) PbO₂^{0.025(60 min)}

other conditions stayed the same, the decomposition of the electrode occurred at around 40 h, which means that the stability was reduced with the increasing *CD* (Figure 4, curve b).

In the case of the lowest *CD* (0.025 A cm⁻²) used for both the BaTiO₃ and PbO₂ depositions for 30 min and 60 min, respectively, the stability increased to 180 h (Figure 4, curve c). By keeping the BaTiO₃ *CD* of 0.025 A cm⁻² and changing the PbO₂ *CD* to 0.1 A cm⁻² over 60 min, the stability of the prepared electrode tremendously decreased to 20 h, as observed in Figure 4, curve d. Finally, only the PbO₂ electrode deposited at the *CD* of 0.025 A cm⁻² in 60 min, showing a stability of 48 h (Figure 4, curve e) explains a high influence of the BaTiO₃ layer on the stability of the PbO₂ electrode.

4 CONCLUSIONS

We successfully investigated an electrodeposition of BaTiO₃ and PbO₂ on Ti using the layer-by-layer method under different conditions. The weight measurement confirms that the BaTiO₃ and PbO₂ formation is optimum at a moderate *CD* of 50 A cm⁻² and a deposition time of 30–45 min. In addition, CV results confirm the same finding through the redox behavior of PbO₂. SEM and XRD results further prove that a moderate *CD* leads to crystalline BaTiO₃ and β-PbO₂ rather than α-PbO₂. The layer-by-layer deposition of BaTiO₃ and PbO₂ makes PbO₂ more stable than it would be if there was only PbO₂. A further application of the selectively prepared electrode is in progress.

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