



# An Application of Conducting Polymer Polypyrrole for the Design of Electrochromic pH and CO<sub>2</sub> Sensors

Vilma Ratautaite,<sup>1</sup> Gintautas Bagdziunas,<sup>1,2</sup> Arunas Ramanavicius,<sup>1,2</sup> and Almira Ramanaviciene<sup>1,z</sup>

<sup>1</sup>NanoTechnas – Center of Nanotechnology and Materials Science, Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Vilnius LT-03225, Lithuania

<sup>2</sup>Department of Material Science and Electrical Engineering, Laboratory of Nanotechnology, Center for Physical Sciences and Technology, Lithuania

In this research, conducting polymer – polypyrrole (Ppy), was electrochemically polymerized on the indium tin oxide coated glass (glass/ITO) electrode. The adhesion of Ppy on the surface of ITO was improved by modification with triethoxymethylsilane (TEMS). Potential cycling was applied for electrochemical deposition of Ppy layer and cyclic voltammograms were recorded during the deposition to monitor polymerization process. Cyclic voltammetry and the potential pulse sequence (PPS)-based chronoamperometry methods complemented the registration of absorbance spectra of glass/ITO(TEMS)/Ppy at various pH and different concentrations of CO<sub>2</sub>. The applicability of glass/ITO(TEMS)/Ppy electrode in the design of electrochromic sensor sensitive toward CO<sub>2</sub> has been evaluated. Cyclic voltammetry based experiments at different potential sweep rates in presence and absence of CO<sub>2</sub> were performed in order to evaluate charge transfer phenomenon in glass/ITO(TEMS)/Ppy structure.  
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Electrochemical reduction of carbon dioxide (CO<sub>2</sub>) as greenhouse gas and the transformation of CO<sub>2</sub> into stabile forms dissolved in aqueous solutions is a promising route, which at some extent enable to solve the problems related to the anthropogenic factors and utilization of fossil fuels.<sup>1</sup> The depletion of the natural resources and the increase of CO<sub>2</sub> emissions is very important recent ecological problem. Transition metals such as Cu, Ag, Pd, Au, Co and their derivatives (i.e., metal oxides and complexes) are the most commonly used catalysts applied for the electrochemical reduction of CO<sub>2</sub>.<sup>2-4</sup>

Conducting polymer – polypyrrole (Ppy), has been employed for various electrochemical applications such as a development of molecularly imprinted polymers,<sup>5,6</sup> humidity sensors<sup>7</sup> and many others analytical systems.<sup>8</sup> Moreover, Ppy is very common object in many electrochemical studies because it is easily synthesizable by chemical or electrochemical methods. On the other hand, it was demonstrated that CO<sub>2</sub> can be electrocatalytically converted into formaldehyde, formic acid and acetic acid at electrode potentials over  $-0.4$  V vs Ag/AgCl<sub>(3M KCl)</sub> on a Ppy-coated electrode under a high pressure in a methanol/LiClO<sub>4</sub> electrolyte-based system.<sup>8</sup> Moreover, the composition of Ppy with metal-organic complexes, metal alloys and metal-based Schiff-bases (e.g., cobalt(II)-based Schiff-base),<sup>9</sup> cobalt-phthalocyanine,<sup>10</sup> nickel complex with 1,4,8,11-tetraazacyclotetradecane,<sup>11</sup> *fac*-Re(2,2'-bipyridine)(CO)<sub>3</sub>Cl,<sup>12</sup> rhenium and copper-rhenium alloys,<sup>13</sup> p-ZnTe<sup>14</sup> as electrocatalysts has provided an alternative route to the electrochemical reduction of CO<sub>2</sub>.

Doped and undoped Ppy layers have been used in the design of pH sensors. During the action of Ppy-based sensors, ion dopant from electrolyte alternates a response of sensor to pH changes. Moreover, analytical signal of Ppy-based sensors depends on a type of anion in the electrolyte.<sup>15</sup> In the presence of weak acid anions such as phthalates, oxalates and salicylates, which can be entrapped during an electrochemical deposition of Ppy layer on the electrode, Ppy-based films have been characterized by faster responses toward the pH changes.<sup>15</sup> Other important feature of the Ppy-based film is the ability to generate from sub- to near-Nernstian electrochemical responses. However, for the Ppy-modified electrodes, the polymer oxidation or reduction processes are coupled with proton uptake. The behaviour of Ppy-modified electrodes, which is based on the proton as a potential determining ion, can be described by the same formalism as it is described for traditional second type electrodes. Experimentally observed small difference from theoretically calculated slope may be caused by the influence of other ions, which are present in the solution.<sup>16</sup> The efficiency of the Ppy-based pH sensors depends also on the thickness of Ppy

layer. Potentiometric response of electrode modified by the thicker Ppy film toward different pHs is non-linear, while the response of the electrode modified with thin Ppy layer toward the pH changes is linear in very broad pH range from pH 2.0 to pH 11.<sup>16,17</sup> However, it should be taken into account that the response time of Ppy modified electrodes is relatively long and is in the range of 1–2 min.<sup>18</sup> Moreover, at room temperature the sensitivity of  $-43.2$  mV/pH of the electrode modified with Ppy layer has been reported.<sup>19</sup> The evaluation of reusability of Ppy-based sensors to the variation of pH strongly depends on parameters applied for reconditioning of the sensors.<sup>20</sup> However, the same authors have reported that neither high pH solutions nor other anion containing electrolytes are suitable for the efficient reconditioning of the Ppy film.<sup>20</sup>

Properties of Ppy-based potentiometric pH sensors significantly depends on the doping of Ppy. In addition, the properties of the doped Ppy also can be improved by adding of some co-dopants. For comparison with other Ppy-based pH electrodes reported previously, the hydroquinone monosulfonate-doped Ppy electrode shows a significantly improved slope of potentiometric response, reduced response time, increased reproducibility and stability.<sup>21</sup> If the oxalate is used as a co-dopant of Ppy, the improvements are more significant.<sup>22</sup>

Ppy, as well as other conducting polymers like polyaniline<sup>23,24</sup> and polyazines<sup>25-27</sup> can be deprotonated. Due to these changes, the electrical and optical properties are observed as a result of decrease of charge density along the polymer chains.<sup>16</sup> Therefore, Ppy possesses the well-defined electrochromic properties.<sup>28</sup> The most important three parameters of the electrochromic polymers are: (1) high optical contrast between its extreme states, (2) short response time and (3) good stability. Among other conducting polymers, Ppy-based polymers have intensively been investigated due to a low price of pyrrole as a monomer, a relatively low oxidation potential, and simple tuning of formed film characteristics by doping with selected ions. Other often-used methods for the modification of optoelectronic properties of Ppy are a copolymerization with several types of monomers and an application of monomers with different types substituting groups on the pyrrole ring.<sup>28</sup>

Electrochromic properties of the Ppy in the potential range from  $-1.0$  V up to  $+1.5$  V vs Ag/AgCl have been demonstrated.<sup>29</sup> It was determined that during the irreversible oxidation of Ppy the conductivity of the polymer decreases not only due to distortion of  $\pi$ - $\pi$  conjugated system, but also due to the loss of electrochemically active sites by the oxidation and degradation of pyrrole moieties in the polymer structure. Moreover, the transmittance changes at wavelengths of 500 nm and 800 nm during the potential cycling indicate an important structural change in the polymer film. The overoxidation very significantly affects the regeneration-ability of Ppy-based layers.<sup>29</sup> However, a

<sup>z</sup>E-mail: almira.ramanaviciene@chf.vu.lt

depletion of some electrochromic properties after consecutive switching is observed in the conjugated polymers based devices.<sup>30</sup> Therefore, the electrochromic properties of the Ppy film are not always successfully recovered in long-term experiments. The obtained Ppy films can exhibit different stability to variation of pH and electrical potential.<sup>30</sup> Moreover, the oxidation and reduction processes of the Ppy film in polymer electrolyte are not completely reversible.<sup>31</sup> Several methods for increasing the stability of the obtained Ppy electrochromic properties has been suggested.<sup>32–34</sup> The electrolyte composition is one of the fundamental parameters, which is changing the stability of Ppy film.<sup>33</sup> Significant enhancement of optical contrast, electrical and optical stability of the polymer in the choline chloride- and/or urea based deep eutectic solvent vs a conventional electrolyte solution have been registered. Synthesis temperature of Ppy doped with gold nanoparticles on fluorine doped tin oxide affects the optical contrast of formed films.<sup>33</sup> The lower synthesis temperature allowed better chain ordering, higher adherence to the substrate and lower thickness, allowing better charge transport during the doping/undoping process.<sup>34</sup>

The aim of this research is to show the applicability of conducting polymer Ppy films electrochemically synthesized on TEMS treated glass/ITO electrode in the design of electrochromic pH and CO<sub>2</sub> sensors.

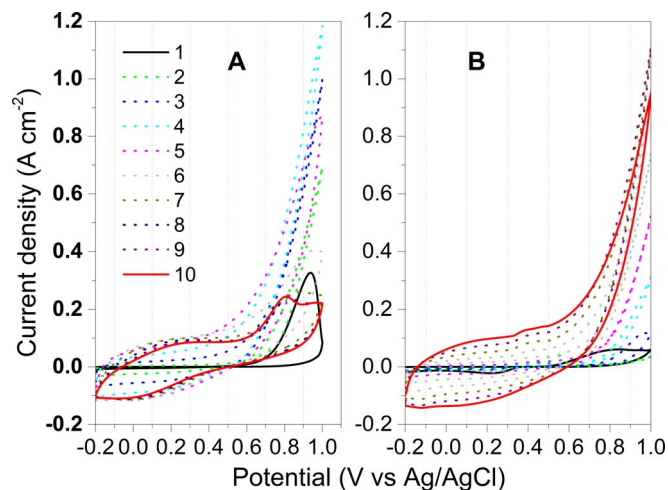
## Experimental

**Chemicals and instrumentation.**—All the chemicals were of analytical grade and were used as obtained except pyrrole, which was purchased from Sigma-Aldrich (Steinheim, Germany) and distilled before the use. Ultra-pure H<sub>2</sub>O was prepared with Adrona Crystal 7 water purification system and a conductivity of purified water, which was used for the preparation of all here used solutions, was of 0.055 μS/cm. Britton – Robinson buffer (BRB)<sup>35</sup> was made of 0.01 M boric acid, 0.01 M acetic acid and 0.01 M phosphoric acid purchased from Scharlau (Sentmenat, Spain), Carl Roth, (Karlsruhe, Germany) and from Fluka, (Buchs, Germany). Ionic strength of BRB solution was supported with 0.1 M LiClO<sub>4</sub> received from Alfa Aesar, (Kandel, Germany). The required pH value of BRB was adjusted with 1.0 M NaOH purchased from Merck (Darmstadt, Germany). Triethoxymethylsilane (TEMS) 99% was purchased from Sigma-Aldrich (Steinheim, Germany). NaHCO<sub>3</sub> was purchased from Alfa Aesar (Kandel, Germany).

**Pretreatment and modification of indium tin oxide coated glass electrode.**—Glass/ITO electrode with surface resistivity of 15–25 Ω/sq was purchased from Sigma-Aldrich (Steinheim, Germany). Before the deposition of conducting polymer by electrochemical polymerization, the glass/ITO surface was cleaned in several steps. Firstly, glass/ITO was washed with ultra-pure water and then immersed in the solution consisting of 27% NH<sub>4</sub>OH and 30% H<sub>2</sub>O<sub>2</sub> mixed at ratio 3:1 and preheated up to 50°C for the 5 min. After that, glass/ITO was cleaned in ultrasonic bath subsequently in water, acetone and water for 15 min in each liquid.

The modification of glass/ITO surface with silane was performed in 4% (v/v) solution of TEMS in acetone overnight and correspondingly TEMS modified structure (glass/ITO<sub>(TEMS)</sub>) was formed. Residues of non-reacted silane were washed with acetone and ultra-pure water. Glass/ITO<sub>(TEMS)</sub> electrode was dried with argon.

**Electrochemical deposition of polypyrrole layer.**—The electrochemical polymerization of pyrrole and all electrochemical measurements were carried out using a computer-controlled potentiostat/galvanostat PGSTAT 128N with Nova 1.10 software received from Eco-Chemie (Utrecht, The Netherlands). Glass cuvette (H × W × D = 32 mm × 30 mm × 18 mm) was used as an electrochemical cell. Pyrrole was polymerized electrochemically on glass/ITO or glass/ITO<sub>(TEMS)</sub> electrode surface from a solution containing 10 mM of pyrrole and 0.1 M of LiClO<sub>4</sub> as an electrolyte and correspondingly glass/ITO<sub>(bare)</sub>/Ppy or glass/ITO<sub>(TEMS)</sub>/Ppy were formed. The Ag/AgCl<sub>(3M KCl)</sub> reference electrode and a platinum wire as a counter electrode were used in the electrochemical deposition of Ppy layer.



**Figure 1.** Cyclic voltammograms registered during the Ppy formation process on glass/ITO<sub>(bare)</sub> (A) and glass/ITO<sub>(TEMS)</sub> (B) electrodes.

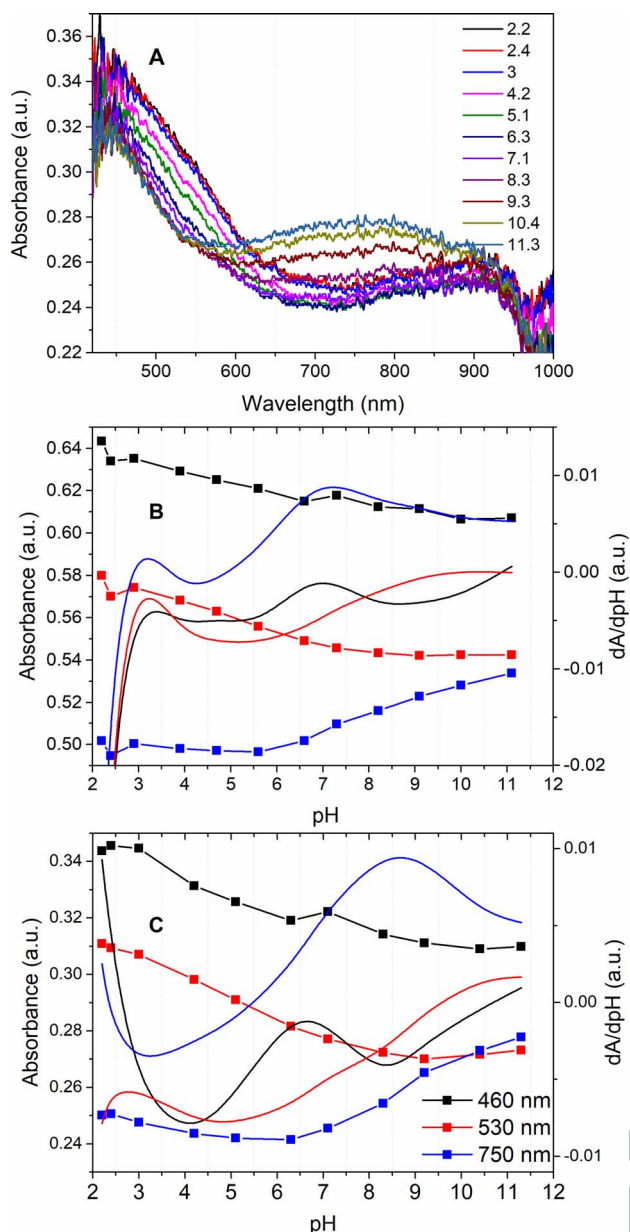
Polymerization was performed in room temperature by 10 potential cycles in the range from –0.2 V to +1.0 V vs Ag/AgCl<sub>(3M KCl)</sub> at the sweep rate of 50 mV/s and step potential of 2.44 mV.

**Evaluation and application of glass/ITO<sub>(bare)</sub>/Ppy and glass/ITO<sub>(TEMS)</sub>/Ppy electrodes for the design of electrochromic pH and CO<sub>2</sub> sensors.**—The evaluation of glass/ITO<sub>(bare)</sub>/Ppy and glass/ITO<sub>(TEMS)</sub>/Ppy characteristics at different pHs was performed in a glass cuvette. The increase of BRB solutions pH after the addition of NaOH was registered with pH-meter. The optical measurements were performed with a spectrometer USB4000-FL equipped by ‘SpectraSuite’ software, both purchased from Ocean Optics (Largo, USA).

UV-Vis absorption spectra were registered at each pH value of BRB solution and the continuous measurements of the absorbance at particular wavelengths (460 nm, 530 nm and 750 nm) vs time were performed. The evaluation of the applicability of glass/ITO<sub>(bare)</sub>/Ppy and glass/ITO<sub>(TEMS)</sub>/Ppy electrodes for the design of electrochromic CO<sub>2</sub> sensors based on cyclic voltammetry and potential pulse alternation methods was performed. Potential of electrode using cyclic voltammetry method was swept from –1.0 V to +0.2 V at 50 mV/s potential sweep rate in BRB solution, pH 2.3, in the presence of different concentrations of NaHCO<sub>3</sub>. Absorbance at 530 nm and 750 nm wavelengths vs time profile were registered during a potential alternation from –0.9 V to +0.2 V in the BRB solution, pH 2.3.

## Results and Discussions

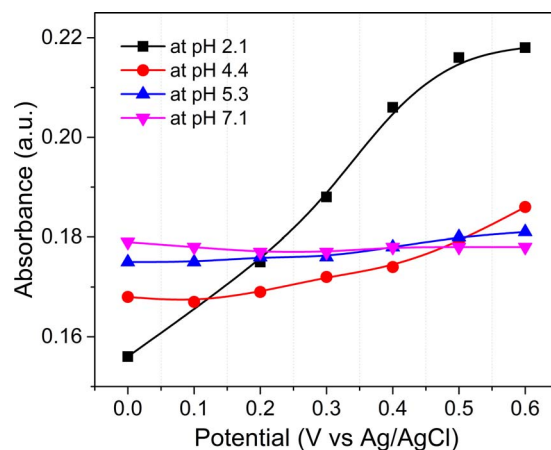
It was determined that formed Ppy film is stable enough to be used in short-term experiments. However, the Ppy-based layer can be significantly degraded by rigorous stirring during the measurements and/or measurement takes longer time that has a negative effect on an analytical signal. The stability of Ppy layer deposited on ITO surface was improved by pre-modification of ITO surface by silane-based interlayer. According to our best knowledge, there are only few researches, which are reporting modification of ITO surface by epoxysilane compound (3-glycidyloxypropyl trimethoxysilane)-based layer, in order to improve the adhesion of Ppy layer on ITO surface.<sup>36–39</sup> For intended application of Ppy layer in the design of electrochromic analytical system, the electrochemical polymerization of Ppy by potential cycling on the glass/ITO electrode (glass/ITO<sub>(bare)</sub>) or on the glass/ITO modified with TEMS electrode (glass/ITO<sub>(TEMS)</sub>) was performed and cyclic voltammograms (CV) were recorded (Fig. 1). First of all, from the 1<sup>st</sup> CV’s cycle registered during the modification of glass/ITO or glass/ITO<sub>(TEMS)</sub> electrodes, it was determined that the electrochemical



**Figure 2.** UV-vis absorbance spectra of glass/ITO<sub>(bare)</sub>/Ppy at different solution pH values (A) and the absorption change of glass/ITO<sub>(bare)</sub>/Ppy (B) and glass/ITO<sub>(TEMS)</sub>/Ppy (C) at 460, 530 and 750 nm. First derivatives of absorbance at different wavelengths with respect to pH (dA/dpH) are presents as solid lines of corresponding color.

218 polymerization of pyrrole started at 0.53 and 0.70 V vs Ag/AgCl<sub>(3M KCl)</sub>  
 219 electrode, respectively. Secondly, the electrical conductivity of the Ppy  
 220 layer deposited on the glass/ITO<sub>(bare)</sub> starts to decrease after the fourth  
 221 potential cycle although the thickness of Ppy layer has increased. How-  
 222 ever, this effect is not observed on the glass/ITO<sub>(TEMS)</sub>/Ppy electrode.  
 223 Here discussed results illustrate that the differences in the conductivity  
 224 of Ppy layers formed on glass/ITO<sub>(bare)</sub> and glass/ITO<sub>(TEMS)</sub> electrodes  
 225 are significant.

226 To evaluate an impact of pH on the Ppy layer, the UV-vis spectra  
 227 in the pH range from pH 2.0 to pH 11.0 were registered (Fig. 2). Such  
 228 pH range was selected taking into account that the conductivity of  
 229 Ppy in the oxidized form is pH-dependent with resistance increasing  
 230 significantly above pH 12.0.<sup>15</sup> Typical profile of the pH impact on  
 231 optical absorbance of Ppy is divided into two regions (Fig. 2). In 1<sup>st</sup>  
 232 region from 450 nm to 600 nm, the optical absorbance decreases, while



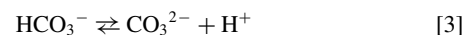
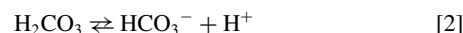
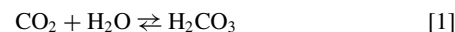
**Figure 3.** Electrochromic properties of glass/ITO<sub>(TEMS)</sub>/Ppy electrode at different pH values of BRB solution. Absorption changes at 750 nm wavelength changing electrode potential were registered.

233 pH is changed from acidic to alkaline. In 2<sup>nd</sup> region from 600 nm to  
 234 900 nm with a maximum at around 750 nm, the absorbance increase  
 235 at same pH interval. Ppy in acidic media has a violet-blue color, while  
 236 this layer in alkaline media has a red-brownish color. Lange et al.<sup>16</sup>  
 237 have declared that the absorbance between 600 and 900 nm increases  
 238 using solutions from pH 6.0 to pH 12.0, while the minimum of the  
 239 absorbance is shifted from 600 nm (at pH 6.0) to 500 nm (at pH  
 240 12.0) due to the deprotonation of the Ppy chains. The same authors  
 241 have claimed that due to deprotonation the absorbance minimum was  
 242 shifted from 710 nm (at pH 7.0) to 570 nm (at pH 11.3).<sup>16</sup>

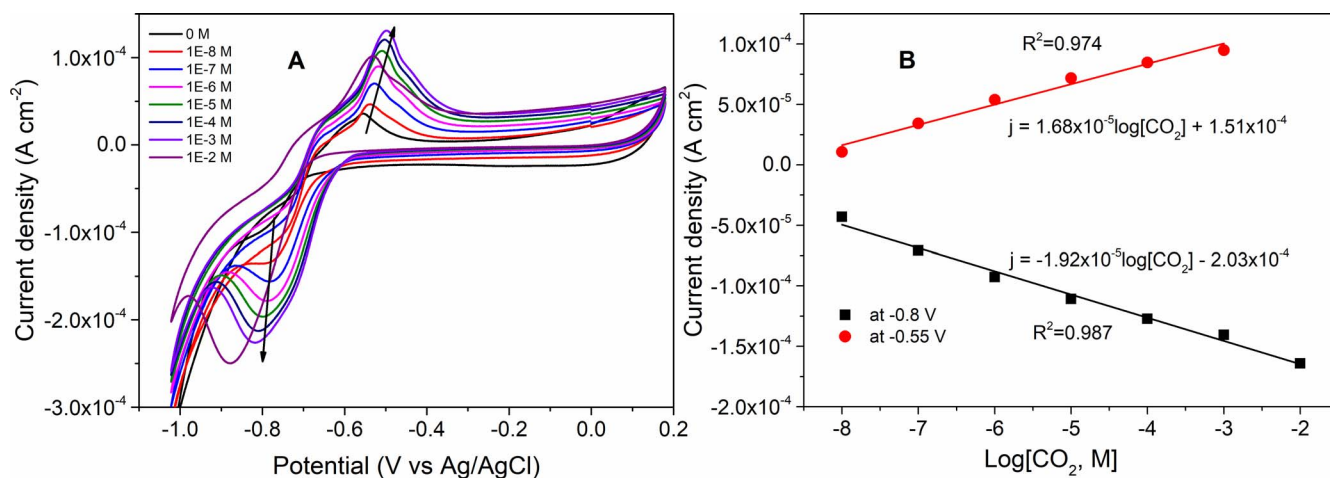
243 For the calculation of pK<sub>a</sub> values of Ppy, first derivative of absor-  
 244 bance with respect to pH (dA/dpH) was applied. According to the  
 245 optical absorbance at 750 nm, which is shown in Figure 2, the pK<sub>a</sub> val-  
 246 ues of Ppy were estimated to be 7.2 for glass/ITO<sub>(bare)</sub>/Ppy and 8.5 for  
 247 glass/ITO<sub>(TEMS)</sub>/Ppy, respectively. The most pH-dependent Ppy forms  
 248 are formed in two pH-ranges of 2–4 and 9–11. According to measure-  
 249 ments of optical absorbance at 650 nm, the pK<sub>a</sub> value of Ppy has been  
 250 estimated as 8.7.<sup>16</sup>

251 Changes of the Ppy layer optical absorbance at 750 nm by changing  
 252 potential of the electrode were registered at several pH values of BRB  
 253 buffer (Fig. 3). The potential of glass/ITO<sub>(TEMS)</sub>/Ppy electrode was  
 254 changed from 0 V to +0.6 V vs Ag/AgCl<sub>(3M KCl)</sub> electrode. Significant  
 255 changes of the absorbance of glass/ITO<sub>(TEMS)</sub>/Ppy in BRB solution, pH  
 256 2.1 were observed during the alteration of the potential. When the pH  
 257 of BRB solution was increased, the changes of Ppy layer absorbance at  
 258 750 nm became negligible. At pH 10, glass/ITO<sub>(TEMS)</sub>/Ppy electrode  
 259 did not showed any electrochromic effect (the data are not shown).  
 260 According to the registered data of optical absorbance changes vs  
 261 applied voltage at the several different pH values in a range from pH  
 262 2.0 to pH 12, the acidic media is the most relevant for the establishment  
 263 of electrochromic properties of Ppy.

264 In order to apply this conducting polymer for the design of electro-  
 265 chromic CO<sub>2</sub> sensor, the BRB solution was supplemented with  
 266 NaHCO<sub>3</sub>. There is an equilibrium between CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>  
 267 in CO<sub>2</sub> saturated solution:



270  
 271 According to presented equations (Eqs. 1–3), the bicarbonate ions  
 272 at pH 2.3 mainly turns into the CO<sub>2</sub> form. Therefore, in this re-  
 273 search bicarbonate ions were used as a source of CO<sub>2</sub>, which is



**Figure 4.** (A) Cyclic voltammograms of glass/ITO<sub>(TEMS)</sub>/Ppy in the presence of different concentrations of CO<sub>2</sub>. (B) The relationships between cathodic and anodic peaks current densities at different CO<sub>2</sub> concentrations. Potential of electrode was cycled from  $-1$  V to  $+0.2$  V at  $50$  mV/s potential sweep rate in BRB solution, pH 2.3.

formed in acidic media. The reduction of CO<sub>2</sub> was performed on the glass/ITO<sub>(TEMS)</sub>/Ppy electrode in the BRB solution, pH 2.3, which contains different concentrations of NaHCO<sub>3</sub>. Figure 4 illustrates that the anodic and cathodic current peaks increased when NaHCO<sub>3</sub> concentration was changed from  $10$  nM until  $10$  mM and in addition, these peaks has shifted. The electrochemical reactions of CO<sub>2</sub> and corresponding electrochemical potentials are summarized in Table I. In cyclic voltammograms, two characteristic peaks were observed, one – anodic at  $-0.55$  V and second – cathodic at  $-0.8$  V ( $1$   $\mu$ M NaHCO<sub>3</sub> in BRB, pH 2.3) (Fig. 4). It corresponds to the chemical reaction presented in equation 5 and oxidation/reduction processes of the Ppy polymer. Moreover, a linear relationship between the cathodic peak current at  $-0.8$  V and the anodic peak current at  $-0.55$  V vs concentration of added NaHCO<sub>3</sub> has been determined (Fig. 4B).

The potential pulse sequence (PPS) method was applied for the evaluation of glass/ITO<sub>(TEMS)</sub>/Ppy based electrochromic sensor used for the determination of CO<sub>2</sub>. The PPS profile was set as: high potential was  $+0.2$  V vs Ag/AgCl<sub>(3M KCl)</sub> and low potential was  $-0.9$  V vs Ag/AgCl<sub>(3M KCl)</sub>, the duration of each potential pulse was  $60$  s. Absorbance of glass/ITO<sub>(TEMS)</sub>/Ppy at the wavelengths  $530$  and  $750$  nm vs time were registered. The absorbance at the  $530$  nm and  $750$  nm wavelengths of glass/ITO<sub>(TEMS)</sub>/Ppy vs time was registered during the continuous measurements (Fig. 5A). The calibration curve representing dependence of absorbance vs  $\log[\text{CO}_2, \text{M}]$  obtained at wavelength  $750$  nm has higher  $R^2$  value in comparison to that obtained at  $530$  nm (Figs. 5B). However, the linear relationship of analytical signal, which was obtained by the cyclic voltammetry-based experiments, vs concentration of CO<sub>2</sub> was better in comparison to here addressed electrochromic method. Despite of this fact, from the calibration curves obtained by using these two methods (Figs. 4B and 5B), the conclusion can be drawn that glass/ITO<sub>(TEMS)</sub>/Ppy electrode in BRB solution, pH 2.3, can be used as the electrochromic CO<sub>2</sub> (or bicarbonate ion) sensor.

To gain insight into charge transfer phenomenon in more detail, the cyclic voltammetry experiments at different glass/ITO<sub>(TEMS)</sub>/Ppy electrode potential sweep rates were performed (Fig. 6). This experiment was carried out in BRB, pH 2.3, containing  $0.1$  M of KCl in the presence (Fig. 6A) and absence (Fig. 6B) of  $0.1$  mM of NaHCO<sub>3</sub>. When potential sweep rates from  $25$  mV s<sup>-1</sup> to  $500$  mV s<sup>-1</sup> were applied, it was observed that by increasing potential sweep rate the cathodic peak potentials at around  $-0.8$  V were shifted to more negative potential values and the anodic peak potentials at around  $-0.5$  V were shifted toward more positive potential values. First of all, from the analysis of plotting the cathodic and anodic peak current vs square root of a scan rate, a good linearity ( $R^2$  of  $0.996$  and  $0.998$ , respectively) was observed. Figure 6C shows that the relationships of the current density vs square root of potential sweep rates are linear and they do not depend on the diffusion of CO<sub>2</sub>. It shows that a polarization and current of the electrode are limiting only a transfer of charge within the Ppy layer or/and through double layer between electrolyte and Ppy. Secondly, the kinetic features of charge transfer, which are estimated experimentally from the plot of anodic peak potential ( $E_{pa}$ ) or cathodic peak potential ( $E_{pc}$ ) versus  $\ln v$ , according to the Laviron's equation, are represented for the cathodic (Eq. 10) and anodic (Eq. 11) processes:<sup>41</sup>

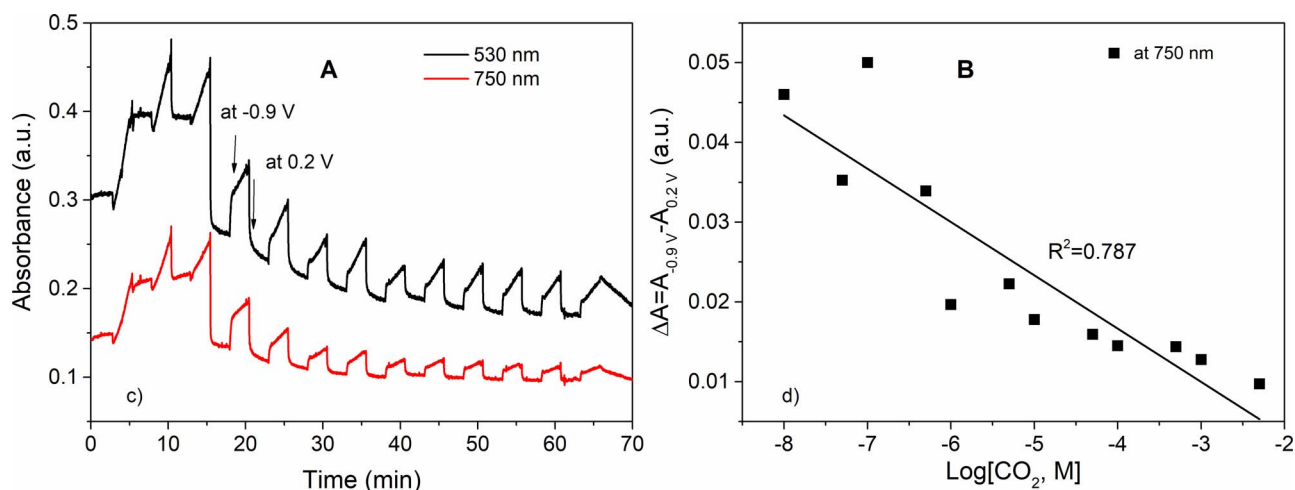
$$E_{pc} = E'^0 + \frac{RT}{\alpha nF} \ln \frac{RTk_{ct}}{\alpha nF} - \frac{RT}{\alpha nF} \ln v \quad [10]$$

$$E_{pa} = E'^0 - \frac{RT}{\beta nF} \ln \frac{RTk_{ct}}{\beta nF} + \frac{RT}{\beta nF} \ln v \quad [11]$$

where  $R$  is an ideal gas constant,  $T$  is an absolute temperature ( $293$  K),  $k_{ct}$  is a charge transfer rate constant,  $n$  is a number of charge,  $F$  is Faraday constant,  $\alpha$  is the charge-transfer coefficient,  $E'^0$  is formal potential (i.e., approximately equal to potential at the scan rate of  $25$  mV s<sup>-1</sup>). The amount of passed charge (expressed by number electrons or holes)

**Table I.** potentials of CO<sub>2</sub> reduction into various products.<sup>40</sup>

Electrochemical reaction	$E^0$ vs Ag/AgCl <sub>(3M KCl)</sub>	Equation No
$\text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	$-0.74$ V	(Eq. 4)
$\text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{HCO}_2\text{H}$	$-0.82$ V	(Eq. 5)
$\text{CO}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	$-0.69$ V	(Eq. 6)
$\text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	$-0.59$ V	(Eq. 7)
$\text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$	$-0.45$ V	(Eq. 8)
$2\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{C}_2\text{O}_4(\text{aq})$	$-1.1$ V	(Eq. 9)



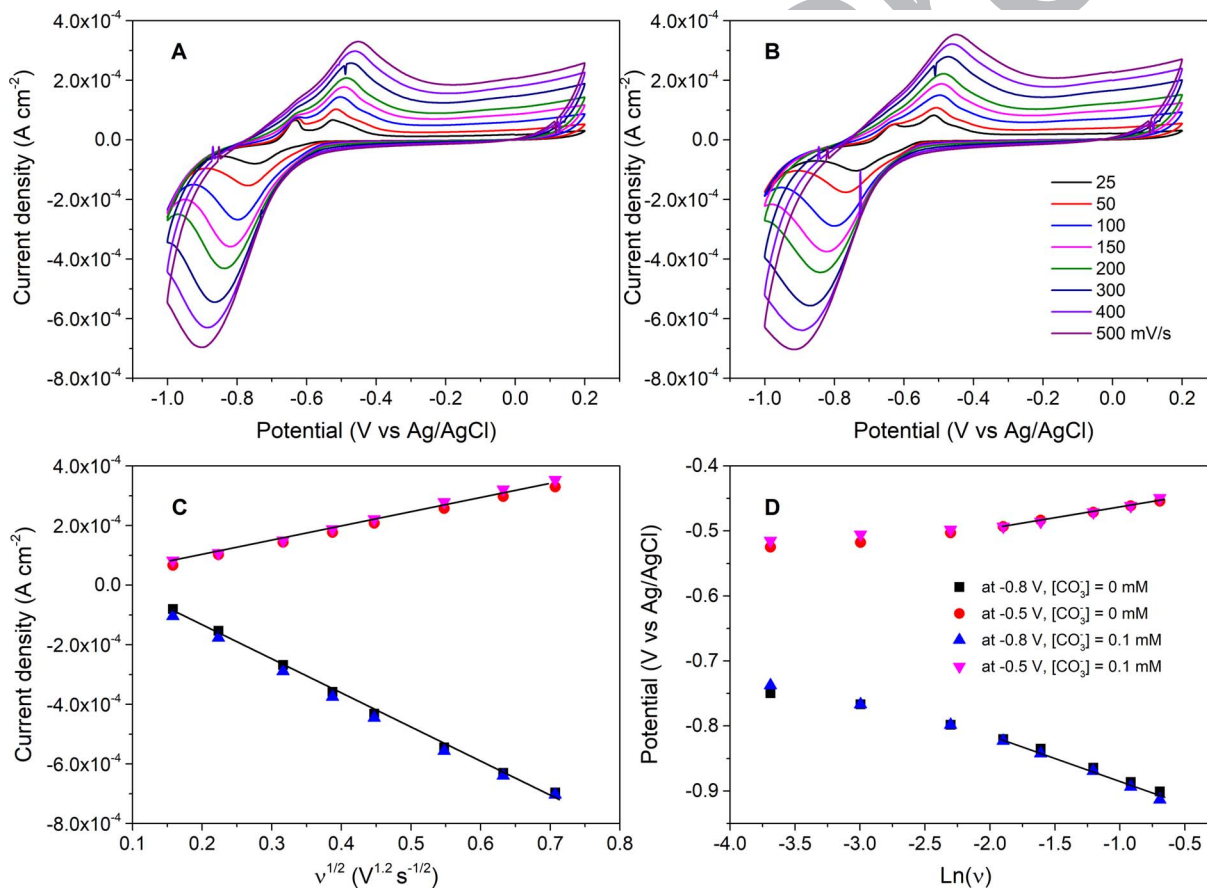
**Figure 5.** The evaluation of glass/ITO<sub>(TEMS)</sub>/Ppy as electrochromic sensor for the determination of CO<sub>2</sub>. Absorbance at wavelengths of 530 nm and 750 nm vs time profile obtained during a potential alternation from -0.9 V to +0.2 V vs Ag/AgCl<sub>(3M KCl)</sub> (A). The dependence of absorbance at 750 nm wavelength on CO<sub>2</sub> concentration in the BRB solution, pH 2.3, (B).

336 was estimated from the separation of oxidation and reduction peaks  
337 in CVs. It can be determined by the peak full width at half maximum  
338 (FWHM) as it is described by Equation 12:<sup>42</sup>

$$n = \frac{3.53 RT}{FWHM \times F} = \frac{90.6 mV}{FWHM} \quad [12]$$

339 In our research,  $n$  was estimated to be around 2 for the Ppy modified  
340 electrode.

Laviron's plots of peak potential dependences on the natural logarithm of potential sweep rates are demonstrated in Figure 6D. The potentials at sweep rates higher than 100 mV s<sup>-1</sup> are linearly proportional to the natural logarithm of potential sweep rate. From the slope of the potential versus  $\ln v$  lines, the transfer coefficients of  $\alpha = 0.41$  and  $\beta = 0.18$  were calculated for cathodic and anodic processes, respectively. In this case, the small values of  $\alpha$  or  $\beta$  (both < 0.5) are indicating that changes in the structure of Ppy are occur-



**Figure 6.** Cyclic voltammograms registered at different potential sweep rates (from 25 mV/s to 500 mV/s) using glass/ITO<sub>(TEMS)</sub>/Ppy electrode in BRB solution with 0.1 M KCl, pH 2.3, and 0.1 mM NaHCO<sub>3</sub>. Cathodic and anodic peak currents vs scan rate without 0.1 mM NaHCO<sub>3</sub> (A) and with 0.1 mM NaHCO<sub>3</sub> (B); cathodic and anodic peak currents vs square root of scan rate (C); peaks potentials vs natural logarithm of the scan rate (D).

ring when a reduced form of Ppy is oxidized.<sup>43</sup> From the intercept of the corresponding lines, rate constants of charge transfer were calculated to be 640 s<sup>-1</sup> and 320 s<sup>-1</sup> for cathodic and anodic processes, respectively.

### Conclusions

Indium tin oxide (ITO) coated glass based light-transparent electrode was electrochemically modified by polypyrrole using potential cycling as an electrochemical polymer deposition method. Therefore, the adhesion of Ppy on the surface of glass/ITO was improved by ITO surface modification with triethoxymethylsilane monolayer. From the impact of pH on the optical absorbance spectra of the Ppy layer, pK<sub>a</sub> values of Ppy were estimated. The pK<sub>a</sub> value of Ppy formed on bare glass/ITO electrode was of 7.2, while for Ppy formed on TEMS modified glass/ITO electrode the pK<sub>a</sub> value was of 8.5. The evaluation of potential impact on the absorbance of glass/ITO(TEMS)/Ppy in the buffers of different pH demonstrated that Ppy spectra were alternated by potential only in an acidic media. The electrochemical and optical methods based on (i) cyclic voltammetry and (ii) the potential pulse sequence complemented with simultaneous registration of current and optical absorbance spectra of glass/ITO(TEMS)/Ppy electrode can be used for the registration of analytical signal in the presence of CO<sub>2</sub>. The linear relationship of analytical signal vs concentration of CO<sub>2</sub> was determined during the evaluation of cyclic voltammograms. From calibration curves obtained by using these two electrochemical methods, the conclusion can be drawn that the glass/ITO(TEMS)/Ppy electrode at pH 2.3 can be used as the electrochromic CO<sub>2</sub> sensor. The analysis of cathodic and anodic peak currents plots vs square root of a potential sweep rate of cyclic voltammograms registered using glass/ITO(TEMS)/Ppy electrode indicated that charge transfer process is controlled by charge transfer through interphase between electrolyte and Ppy, and through the Ppy layer.

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### ORCID

Gintautas Bagdziunas  <https://orcid.org/0000-0002-9924-6902>

Arunas Ramanavicius  <https://orcid.org/0000-0002-0885-3556>

Almira Ramanaviciene  <https://orcid.org/0000-0001-5864-0359>

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