

# High performance platinized titanium nitride catalyst for methanol oxidation†

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Platinized TiN is shown to be a very good catalyst for the electrochemical oxidation of methanol; it does not contain Ru and the CO poisoning effect is alleviated by the presence of TiN.

Fuel cells have been the focus of interest for the conversion of chemical energy into electrical energy in the past few decades.<sup>1–3</sup> Among the systems being studied, the direct methanol fuel cell has been projected to be useful for portable devices as well as transport applications.<sup>4–7</sup> The most effective and promising catalyst for methanol oxidation is reported to be Pt–Ru loaded on to carbon.<sup>8,9</sup> Pt–Ru shows good performance since the high activity of Pt for methanol oxidation is combined with Ru which alleviates CO poisoning.<sup>10–13</sup> However, the high loading of noble metals, Pt and Ru, has resulted in the search for alternate catalysts.<sup>13</sup> Leaching of Ru is one of the concerns as well.<sup>13,14</sup> Tungsten carbide microspheres deposited with platinum has been recently shown to be a promising material.<sup>15</sup>

Towards this direction, the present communication reports on the use of Pt deposited titanium nitride, for the electrochemical oxidation of methanol. Titanium nitride (TiN) is an extremely hard, conducting ceramic material, often used as a coating for titanium alloys, steel and aluminium components to improve their surface properties.<sup>16,17</sup> It is classified as a “barrier metal” in electronic industries owing to its excellent diffusion barrier properties.<sup>18,19</sup> TiN possesses very good conductivity<sup>19</sup> and it is biocompatible as well.<sup>20</sup> The reported literature on the use of TiN is limited to its use in supercapacitors,<sup>21</sup> as a substrate for electrodeposition of metals such as Pt, Cu, Ag or Zn,<sup>22–24</sup> pH sensor,<sup>25</sup> deactivation of marine bacteria<sup>26</sup> and electroanalysis.<sup>27</sup>

In the present studies, TiN is used as a substrate for Pt deposition and the Pt–TiN is used as an electrocatalyst for methanol oxidation. TiN is coated on stainless steel substrates by cathodic arc deposition (ESI†). The coatings are characterized by powder XRD technique. The electrodes are prepared by attaching a Cu lead to the SS coated TiN by spot welding. The exposed Cu and stainless steel edges are insulated using epoxy resin. The electrochemical measurements are performed in a three electrode cell using Pt–TiN as the working electrode, large area Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the

reference electrode. Pt electrodeposition onto TiN is carried out from 0.1 M H<sub>2</sub>PtCl<sub>6</sub>. The conditions for platinum electrodeposition using chronopotentiometry are given in the ESI†. The amount of platinum loaded onto the TiN surface is 22 μg cm<sup>-2</sup>. The SEM (Fig. 1) and EDX (ESI†) analysis of the platinized TiN reveal that the surface is uniformly covered with Pt electrodeposits. Depending on the conditions used for chronopotentiometric deposition of platinum, the surface is either partially covered or fully covered. The oxidation of methanol has been carried out with different platinum loadings and the results obtained using a partially covered electrode (for a Pt loading of 22 μg cm<sup>-2</sup>) are given here. The control experiment shows that TiN is inactive towards methanol oxidation. Fig. 2 shows the voltammograms obtained with platinized TiN for the oxidation of methanol in H<sub>2</sub>SO<sub>4</sub>. There is a clear oxidation peak observed that grows as a function of number of cycles and there is a small shift in the peak potential towards less positive values. The peak potential in the forward direction is close to that observed for bare platinum electrodes.<sup>28</sup> The peak currents stabilize after 35 cycles and it is found to be stable thereafter without any decrease. The decreasing trend in currents with the number of cycles as observed on other platinized electrodes like Pt coated on glassy carbon (Pt-GC), Pt/Ru-GC, Pt/Sn-GC<sup>29</sup> is not observed in the present case.

The performance of the Pt–TiN can be benchmarked by comparing the ratio of currents in the forward (*I<sub>f</sub>*, anodic direction) and reverse (*I<sub>b</sub>*) scans. A decrease in the ratio of *I<sub>f</sub>*/*I<sub>b</sub>* as a function of number of cycles points out the difficulty and complexity associated with the oxidation of methanol and excessive accumulation of oxidation products on the catalyst surface. Hence, a high *I<sub>f</sub>*/*I<sub>b</sub>* value is indicative of improved CO tolerance. The reported *I<sub>f</sub>*/*I<sub>b</sub>* value for the commercial E-TEK catalyst is ~1.<sup>30,31</sup> The ratio observed for Pt–Ru after vigorous heat treatment, is ~1.30.<sup>31</sup> Pt<sub>52</sub>Ru<sub>48</sub> supported on carbon has

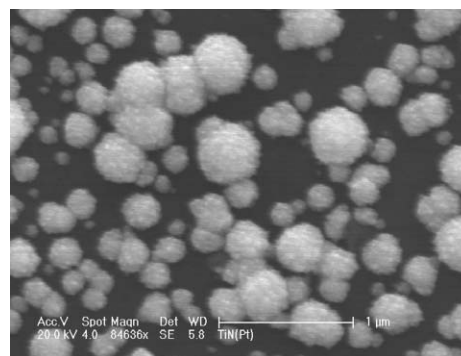
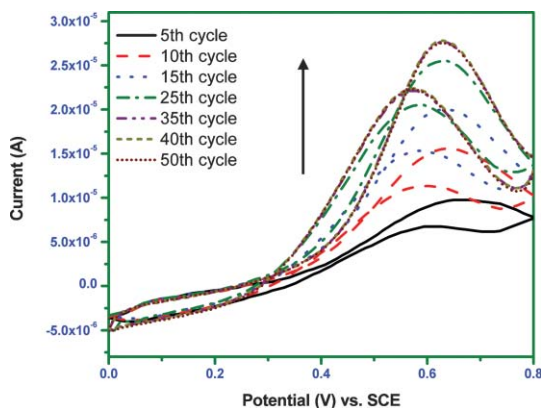


Fig. 1 Scanning electron micrograph of Pt–TiN.

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**Fig. 2** Cyclic voltammograms of Pt–TiN in presence of 0.5 M methanol and 0.5 M sulfuric acid as a function of no. of cycles. The Pt loading is  $22 \mu\text{g cm}^{-2}$  and the scan rate used is  $20 \text{ mV sec}^{-1}$ . Note that the voltammograms for the 35th, 40th and 45th cycles have very little difference in currents.

been reported to exhibit a ratio of 2.30.<sup>32</sup> In the present studies, the ratio is observed to be 1.26 for Pt–TiN without any pre-treatment. Yet another method to assess the catalytic efficiency is the potential separation between the peaks in the forward scan ( $E_f$ ) and that in the reverse scan ( $E_b$ ). The value is  $\sim 200 \text{ mV}$  at a scan rate of  $50 \text{ mV s}^{-1}$  for pure platinum and is the same at  $25 \text{ mV s}^{-1}$  for the commercial E-TEK (20 wt% Pt in Vulcan carbon) catalyst.<sup>30</sup> The value for the activated Pt–Ru/Vulcan carbon system is observed to be  $200 \text{ mV}$ <sup>33</sup> at a scan rate of  $20 \text{ mV s}^{-1}$ . The value observed for Pt–TiN is  $70 \pm 5 \text{ mV}$  at a scan rate of  $20 \text{ mV s}^{-1}$  clearly revealing the advantages associated with the Pt–TiN catalyst.

A growth in peak currents and a positive shift in peak potential with repeated cycling have been reported for Pt–Ru<sup>14</sup> and Pt/RuO<sub>2</sub>·xH<sub>2</sub>O/carbon nanotube<sup>34</sup> systems. The reason for this is suggested to be due to the leaching of Ru from the surface and poor kinetic characteristics of ruthenium oxides, respectively. The Pt coated tungsten carbide microspheres have shown similar behaviour<sup>15</sup> and the possible reason given by the authors is the removal of surface oxygen species as a function of time before a steady state is established.

In the present studies, the electrode Pt–TiN does not contain Ru and hence the reasoning based on leaching of Ru with an increase in the surface area of Pt is ruled out. Secondly, the reflectance infrared spectra (RAIRS) of the Pt–TiN surface before and after methanol oxidation (ESI†) show a large increase in the –OH intensity, supporting the formation of Ti–OH type functional groups. This is similar to the growth in Ru–OH groups in Pt–Ru systems that help in alleviating CO poisoning. Thirdly, a control experiment where the Pt–TiN is conditioned at a positive potential of 0.7 V in sulfuric acid alone does not result in any change as far as the effect of subsequent cycling in methanolic sulfuric acid solution is concerned. This leads to the fact that the activation of the surface to yield high currents probably happens *in situ* during the oxidation of methanol.

It is known that TiN gets oxidized in aqueous sulfuric acid<sup>35</sup> to form oxynitride and oxide species. The oxidation is shown to occur even at 0.6 V (vs. SCE) in a sulfuric acid medium though the extent of oxidation is small. Additionally, the voltammogram of TiN in

sulfuric acid shows a large, sharp peak at about 1.3 V due to the oxidation of the surface. In the case of Pt–TiN, it is very likely that the TiN surface gets oxidized and the product possibly aids the oxidation of methanol by a mediator-type mechanism thereby getting reduced to TiN. The formation of Ti–OH type groups, as inferred from the infrared spectra, improves the efficiency by removing the CO formed during the oxidation of methanol. Other possible reasons could be related to the effect of the support, similar to a metal–support interaction observed in catalytic reactions.<sup>36,37</sup> It is also known that the CO desorption temperature decreases when platinum is loaded onto a support when compared to bare platinum.<sup>15</sup> This may result in reduced poisoning of the Pt surface when it is supported on TiN.

The oxidation peak currents observed after stabilizing the electrode for several cycles vary as the square root of the scan rate (ESI†). The dependence of current on methanol concentration reveals that there is linearity observed up to a certain concentration (ESI†). It should be pointed out that a Pt–TiO<sub>2</sub> electrode has been reported to result in the methanol oxidation currents diminishing as a function of number of cycles.<sup>38</sup> Hence the effect observed on Pt–TiN is not similar to the one on Pt–TiO<sub>2</sub>.

Electrochemical oxidation of other aliphatic alcohols such as ethanol follow a similar trend. But higher aliphatic alcohols, such as propanol and isopropanol, and acids such as HCOOH follow a different trend. Interestingly, the Pt–TiN electrode shows extreme poisoning for HCOOH oxidation that results in a dramatic decrease in the oxidation current as a function of the number of cycles. The reactions involving other small molecules are being probed further.

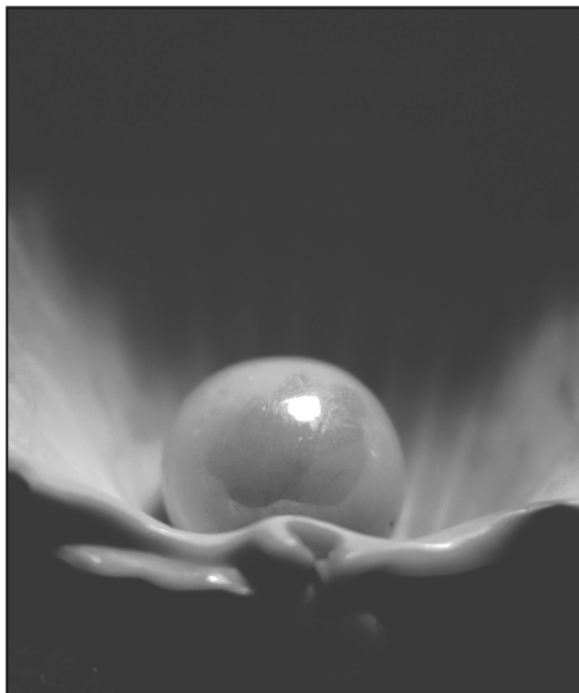
In summary, the present investigations open up the possibility of replacing the precious metal Ru in conventional Pt–Ru system by widely available, stable TiN. The mechanism of oxidation of methanol as well as the increasing trend in currents is being studied using other spectroscopic techniques.

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