

## Transition of oscillatory mechanism for methanol electro-oxidation on nano-structured nickel hydroxide film (NNHF) electrode

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**Instead of CO<sub>ad</sub> formation and removal as on Pt electrodes, coupling of charge transfer with diffusion and convection mass transfer accounts for the oscillation found in the methanol electro-oxidation on the NNHF electrode.**

The mechanism for the electrocatalytic oxidation of methanol, as well as formic acid and formaldehyde, on Pt and Pt-based electrodes has been intensively studied over the past decades,<sup>1–4</sup> owing to their fundamental importance as model systems and potential applications in fuel cells. A variety of *in situ* techniques, such as IR, DEMS, Raman, and so on, have been developed and improved to elucidate the electrocatalytic processes.<sup>1–7</sup> These investigations have deepened our understanding not only of the electrocatalytic processes themselves, but also of the oscillatory reaction kinetics, a closely interrelated interesting subject.<sup>8–9</sup> It has been confirmed that methanol, like formic acid and formaldehyde, is oxidized into CO<sub>2</sub> on Pt *via* a dual-path mechanism, *i.e.* *via* poisoning (CO<sub>ad</sub>) and reactive (*e.g.* HCOO<sup>–</sup>)<sup>6</sup> intermediates. The strongly bonded CO forms on the surface at lower potentials from the dissociative adsorption of the reactant, and it is removed at higher potentials by reacting with chemisorbed water molecules and/or with surface bonded hydroxyl radicals (OH<sub>ad</sub>). These surface steps are responsible for the galvanostatic potential oscillations on Pt in the electro-oxidation of methanol, as well as other one-carbon organic molecules.<sup>8–9</sup> From the point of view of electrode processes, this category of oscillators can be classified into the type of coupling of charge transfer with surface ad- and desorption.<sup>10–11</sup>

In the present study, the electro-oxidation of methanol on a nano-structured nickel hydroxide film (NNHF) electrode has been performed in alkaline solution. A transition in the rate-determining step has been found from the surface step into diffusion mass transfer, due to the high electrocatalytic activity of the NNHF electrode. A new kind of potential oscillation has also been found, belonging to the type of coupling of charge transfer with diffusion and convection mass transfer.<sup>10</sup> This oscillatory mechanism has been testified by electrochemical measurements and *in situ* Raman spectroscopy.

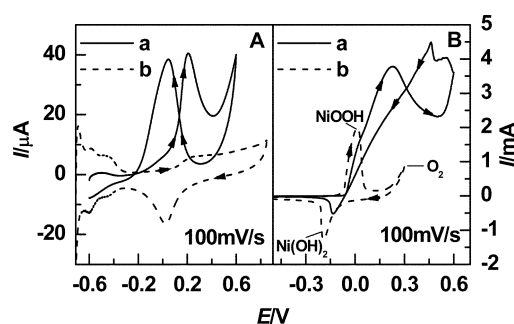
The NNHF electrode served as the working electrode, which was electrodeposited<sup>12</sup> on a mechanically roughened nickel disk (1 mm diameter). The average particle size of the deposit was estimated around 100 nm through AFM images. The same size of polycrystalline Pt electrode was also used for comparison. A platinum wire circle and a saturated mercurous sulfate electrode (SMSE) were employed as the counter and reference electrode, respectively. The *in situ* Raman spectra were obtained with a Renishaw RM1000 confocal microscope. The exciting wavelength was 632.8 nm. A detailed description for Raman measurements can be found elsewhere.<sup>7,13</sup>

Noticeably, crossed cyclic voltammograms (CVs) occur in Fig. 1 for methanol electro-oxidation both on the Pt and on the NNHF electrodes. A crossing loop forms in the CV while the current for the backward scan is larger than that for the forward scan. The crossing loop means that there are two opposite steps, *i.e.* positive and negative feedbacks, overlapping within the bistable states. We found that such a crossing loop can act as a universal criterion for electrochemical oscillatory systems.<sup>10–11</sup> So oscillations can be expected to occur for methanol electro-oxidation on the NNHF

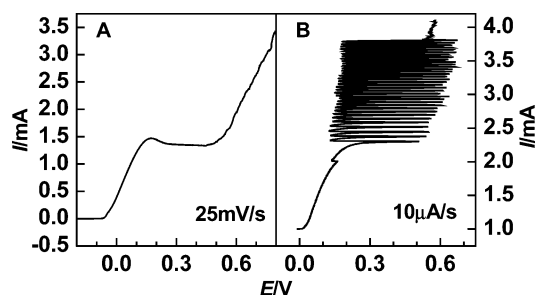
electrode, in addition to on the Pt electrode as reported in the literature.<sup>8–9</sup> The prediction proves to be true (Fig. 2B). It is really exciting that a new oscillator was found by simply taking a CV.

However, the fact that the two crossing loops in Fig. 1A and Fig. 1B locate in different potential ranges indicates that they generate from different kinetics steps, referring to different electrocatalytic and oscillatory mechanisms.

As we can see in Fig. 1A, the crossing loop occurs in the first ascending branch for methanol electro-oxidation on Pt. Surface bonded CO<sub>ad</sub> that forms from methanol dissociation exists at lower potentials. It represses hydrogen ad/desorption and methanol oxidation. So methanol oxidation current in the double layer region is smaller during the forward potential scan. The oxygen species involved in the reaction in the double layer region might originate mainly from the surface adsorbed water molecules.<sup>8–9</sup> CO<sub>ad</sub> can be effectively removed at higher potentials by reacting with OH<sub>ad</sub> that is produced in the oxygen adsorption region. The removal of CO<sub>ad</sub> in this way explains not only the evanishment of the reduction peak of oxygen species that exists in the absence of methanol, but also the larger oxidation current in the double layer region during the backward potential scan. The formation and removal of CO<sub>ad</sub> constitute the main positive and negative feedback steps in the crossing loop, and account for the galvanostatic potential oscillation. Such a mechanism is consistent with the fact that oscillations occur in the first ascending branch where the crossing loop occurs.<sup>11</sup>



**Fig. 1** Cyclic voltammograms on (A) Pt or (B) NNHF electrode for (a) 1 mol dm<sup>–3</sup> CH<sub>3</sub>OH in (A) 1 mol dm<sup>–3</sup> HClO<sub>4</sub> or (B) 1 mol dm<sup>–3</sup> NaOH. The dashed lines of (b) are CVs for the base solutions.

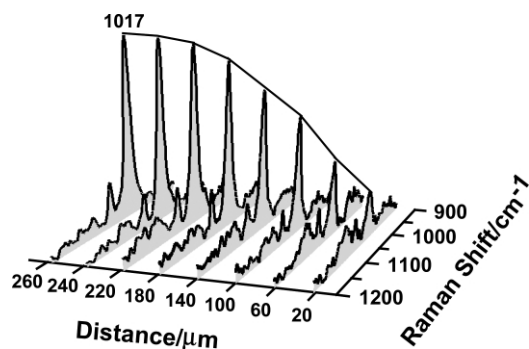


**Fig. 2** Current–potential curves measured by (A) potential and (B) current scanning for 1 mol dm<sup>–3</sup> CH<sub>3</sub>OH oxidation in 1 mol dm<sup>–3</sup> NaOH on the NNHF electrode.

On the nano-structured NNHF electrode, the redox pair of Ni(OH)<sub>2</sub>/NiOOH (curve b in Fig. 1B) act as the electronic mediator in the methanol electrocatalytic oxidation.<sup>14</sup> It can be seen from Fig. 1B that methanol oxidation occurs after the NiOOH formation, and the NiOOH reduction peak diminishes in the presence of methanol. The typical vibration bands from NiOOH (476, 570 cm<sup>-1</sup>), formate (1351, 1382 cm<sup>-1</sup>) and carbonate (1066 cm<sup>-1</sup>) have been detected by *in situ* Raman spectroscopy during the methanol electro-oxidation, but no vibration bands for CO<sub>ad</sub> can be observed. These results are consistent with those from *in situ* FTIR.<sup>15</sup> Instead of CO<sub>ad</sub> formation and removal as on the Pt electrodes, the main surface steps in the methanol electro-oxidation on the NNHF electrode involve the interconversion of Ni(OH)<sub>2</sub> and NiOOH, and the formation of formate and carbonate as the intermediate and final products in alkaline solution depending on the potential. This mechanistic difference can be attributed mainly to the difference in chemistry between Pt and NNHF. The peak current density on the NNHF electrode ( Fig. 1B) is much larger than that on the Pt electrode ( Fig. 1A), indicative of its better electrocatalytic activity for methanol oxidation. The nano structure might also contribute to the higher catalytic activity of the NNHF since its peak current density for methanol oxidation is about ten times as large as that on a bare Ni electrode.

Unlike on the Pt electrode where surface steps are essential, the crossing loop that appears in the descending branch on the NNHF electrode (curve a of Fig. 1B) mainly results from the diffusion and convection mass transfer. The descending branch during the forward potential scan comes from the methanol depletion near the surface by oxidation under limiting diffusion, because a limiting diffusion current plateau appears with a slower potential scan (Fig. 2A). The methanol concentration profile in the diffusion layer is also shown in Fig. 3, which was measured by an *in situ* spatial-resolved Raman spectroscopic technique.<sup>13</sup> The diffusion layer, which can be estimated from Fig. 3, is about 240 μm thick. The larger oxidation current in the backward potential scan (Fig. 1B) is due to the enhanced convection mass transfer of methanol induced by oxygen evolution, because no crossing loops can be observed (not showing) while the potential scan is reversed before the second ascending branch where oxygen evolution occurs. Although such a crossing loop that stems from the diffusion and convection mass transfer has been reported for the reduction (*e.g.* IO<sub>3</sub><sup>-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) or oxidation (*e.g.* Fe(CN)<sub>6</sub><sup>4-</sup>) of some inorganic substances in alkaline media,<sup>10,16</sup> it is the first time for the methanol electro-oxidation.

The oscillatory mechanism for the methanol electro-oxidation on the NNHF electrode also changes into the type of coupling of charge transfer with diffusion and convection mass transfer as we classified.<sup>10</sup> Such a mechanism can be concluded as well from Fig. 2, noticing that the oscillation appears above the limiting current



**Fig. 3** Spatial-resolved *in situ* Raman spectra during the methanol electro-oxidation on NNHF electrode at 0.2 V with a same solution as in Fig. 2. The curve lying at peak 1017 cm<sup>-1</sup> indicates the methanol concentration profile in the diffusion layer.

only and the oscillatory amplitude is within the limiting current plateau range (comparing Figs. 2A with 2B). While the applied current is larger than the limiting current for methanol oxidation, its surface concentration soon depletes to zero due to the limited supplying rate by diffusion. In order to maintain the applied current, the potential moves to the higher potential side of the plateau till oxygen evolution. The growth, detachment and movement of the oxygen bubbles act like an agitator and produce forced convection mass transfer. The methanol surface concentration is thus replenished and the potential shifts to the lower side of the plateau again. This oscillatory mechanism is further confirmed by some other experimental facts. For example, periodic oxygen evolution was observed during the oscillation at the higher potential side, and oscillations disappeared at once upon a constant (rather than periodic) stronger agitation because no depletion can occur. Agitation is an effective method to distinguish the two main types of oscillations classified on the basis of electrode processes,<sup>10</sup> since agitation does not remove the oscillation that mainly involves surface steps. The oscillations that involve convection feedback step<sup>13,16</sup> seem not to fall into the types, *e.g.* N-NDR, H-NDR and S-NDR, defined recently by Krischer<sup>17</sup> on the basis of the *I/E* shape. Note that the steady-state *I/E* shape (Fig. 2A) is a step-like one.

In conclusion, a new oscillator has been found for methanol electrocatalytic oxidation on the NNHF electrode by means of the crossing loop in CV. Instead of the formation and removal of CO<sub>ad</sub> as on the Pt electrode, alternatively dominant diffusion and convection mass transfer plays the key role in the oscillation on the NNHF electrode, owing to its higher electrocatalytic activity. We believe that these new findings will be of great significance not only to better understanding of the methanol electrocatalytic process and its relationship with oscillations, but also in exploiting the electrocatalysts for methanol fuel cells.

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