RSC Advances

Supplementary Data

Fabrication and performance evaluation of a novel membrane electrode assembly for DMFC

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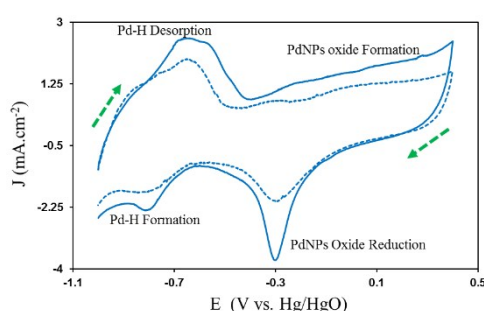
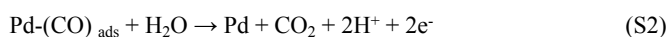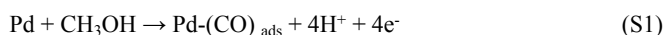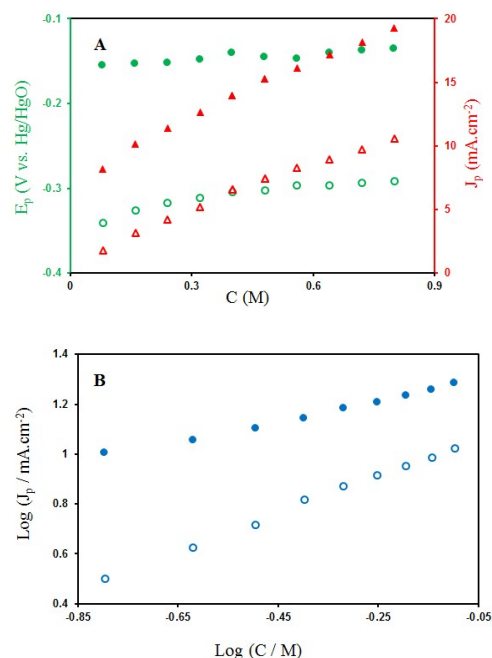**Figure S1.** The cyclic voltammogram of GC/PdNPs-LaNi$_{0.5}$Fe$_{0.5}$O$_3$NPs-CH electrode after 1 (solid line) and 100 (dash line) cycles sweep with the palladium loading of 0.31 mg.cm^{-2} in 1 M KOH aqueous solution at 50 mV.s^{-1}.

Mechanism of methanol oxidation on PdNPs-LaNi$_{0.5}$Fe$_{0.5}$O$_3$NPs-CH nanocomposite

Similar to the mechanism of methanol oxidation on noble metal surface, the following reaction pathway can be proposed:

$$Pd + CH_3OH \rightarrow Pd\text{-}(CO)_{ads} + 4H^+ + 4e^- \quad (S1)$$

$$Pd\text{-}(CO)_{ads} + H_2O \rightarrow Pd + CO_2 + 2H^+ + 2e^- \quad (S2)$$

It seems that the possible reaction pathway of methanol oxidation on the perovskite LaNi$_{0.5}$Fe$_{0.5}$O$_3$ surface in the presence of an alkaline electrolyte be as follows (M^{n+}: La^{3+}, Ni^{2+} and Fe^{3+}):

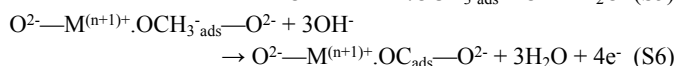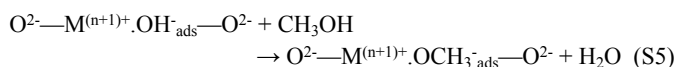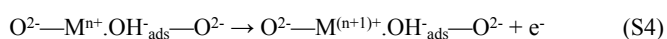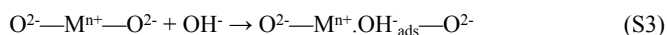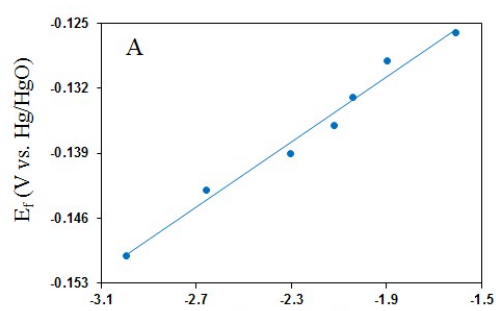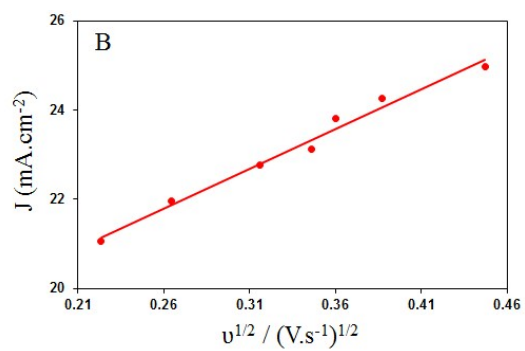$$O^{2-}\text{—}M^{n+}\text{—}O^{2-} + OH^- \rightarrow O^{2-}\text{—}M^{n+}.OH^-_{ads}\text{—}O^{2-} \quad (S3)$$

$$O^{2-}\text{—}M^{n+}.OH^-_{ads}\text{—}O^{2-} \rightarrow O^{2-}\text{—}M^{(n+1)+}.OH^-_{ads}\text{—}O^{2-} + e^- \quad (S4)$$

$$O^{2-}\text{—}M^{(n+1)+}.OH^-_{ads}\text{—}O^{2-} + CH_3OH \rightarrow O^{2-}\text{—}M^{(n+1)+}.OCH_3^-_{ads}\text{—}O^{2-} + H_2O \quad (S5)$$

$$O^{2-}\text{—}M^{(n+1)+}.OCH_3^-_{ads}\text{—}O^{2-} + 3OH^- \rightarrow O^{2-}\text{—}M^{(n+1)+}.OC_{ads}\text{—}O^{2-} + 3H_2O + 4e^- \quad (S6)$$

$$O^{2-}\text{—}M^{(n+1)+}.OC_{ads}\text{—}O^{2-} \rightarrow O^{2-}\text{—}M^{(n+1)+}\text{—} + CO_2 + 2e^- \quad (S7)$$

$$O^{2-}\text{—}M^{(n+1)+}\text{—} + 2OH^- \rightarrow O^{2-}\text{—}M^{(n+1)+}\text{—}O^{2-} + H_2O \quad (S8)$$

$$O^{2-}\text{—}M^{(n+1)+}\text{—}O^{2-} + OH^- \rightarrow O^{2-}\text{—}M^{(n+1)+}.OH^-_{ads}\text{—}O^{2-} \quad (S9)$$

$$O^{2-}\text{—}M^{(n+1)+}.OH^-_{ads}\text{—}O^{2-}+CH_3OH+6OH^- \rightarrow O^{2-}\text{—}M^{(n+1)+}.OH^-_{ads}\text{—}O^{2-}+CO_2+5H_2O+ 6e^- \quad (S10)$$
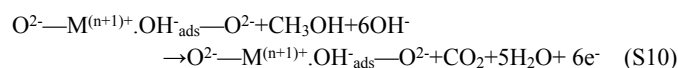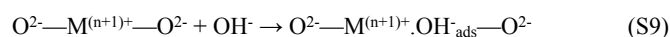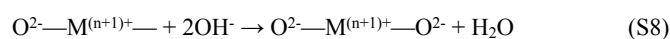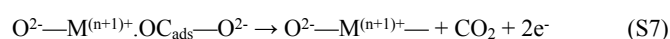
Figure S2. Plot of the (A) effect of methanol concentration on peak potential (○) and current density (Δ) of methanol oxidation and (B) peak current dependence *vs.* the logarithm of methanol concentration at forward (solid) and backward (hollow) sweep on the GC/PdNPs-LaNi$_{0.5}$Fe$_{0.5}$O$_3$NPs-CH electrode in 1 M KOH aqueous solution and 50 mV.s^{-1} scan rate.

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Figure S3. The plot of (A) the anodic peak potential vs. ln υ and (B) the anodic peak current density of methanol oxidation vs. $\upsilon^{1/2}$ on the GC/PdNPs-LaNi$_{0.5}$Fe$_{0.5}$O$_3$NPs-CH electrode in 0.8 M methanol and 1 M KOH aqueous solution at different scan rates: 50 - 200 mV.s^{-1}.