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:

\[
\begin{align*}
\text{Pd} + \text{CH}_3\text{OH} & \rightarrow \text{Pd-(CO)}_{\text{ads}} + 4\text{H}^+ + 4\text{e}^- \quad \text{(S1)} \\
\text{Pd-(CO)}_{\text{ads}} + \text{H}_2\text{O} & \rightarrow \text{Pd} + \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad \text{(S2)}
\end{align*}
\]

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$^{3+}$):

\[
\begin{align*}
\text{O}^2- - \text{M}^{(n+1)+} & \rightarrow \text{O}^2- - \text{M}^{(n+1)+} + \text{CO}_2 + 2\text{e}^- \quad \text{(S7)} \\
\text{O}^2- - \text{M}^{(n+1)+} + 2\text{OH}^- & \rightarrow \text{O}^2- - \text{M}^{(n+1)+} + \text{O}^2- + \text{H}_2\text{O} \quad \text{(S8)} \\
\text{O}^2- - \text{M}^{(n+1)+} & \rightarrow \text{O}^2- - \text{M}^{(n+1)+} + \text{OH}^-_{\text{ads}} - \text{O}^2- \quad \text{(S9)} \\
\text{O}^2- - \text{M}^{(n+1)+} + \text{CH}_3\text{OH} + 6\text{OH}^- & \rightarrow \text{O}^2- - \text{M}^{(n+1)+} + \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- \quad \text{(S10)}
\end{align*}
\]

Figure S2. Plot of the (A) effect of methanol concentration on peak potential ($\nu$) and current density ($\Delta$) 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.
Figure S3. The plot of (A) the anodic peak potential vs. ln $\nu$ and (B) the anodic peak current density of methanol oxidation vs. $\nu^{1/2}$ 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$^{-1}$.