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Characterization of Ni-Prussian blue with Cyanide Vacancies by Synchrotron Radiation (soft X-ray absorption)

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Water oxidation is the thermodynamic and kinetic bottleneck in the process of electrolysis. Consequently, significant efforts have been directed toward finding efficient, affordable (using abundant elements), and stable catalysts. Prussian blue analogs (PBAs) have emerged as efficient catalysts under mild conditions (pH=7), and the performance of oxygen evolution by PBAs can be enhanced by creating cyanide vacancies in the hexacyanometalate complexes. In this study, we investigate the influence of creating cyanide vacancies in nickel-Prussian blue (Ni-PB-vac) catalysts and aim to understand the electronic structure of these catalysts, including both Ni-PB and Ni-PB-vac. For this purpose, we utilized the IPE-Beam line (soft X-ray range: 100–2000 eV) at Sirius, the Brazilian Synchrotron Light Laboratory (LNLS). We analyzed the Fe (Fe^{3+}) and Ni (Ni^{2+}) $L_{2,3}$ edges in Ni-PB and Ni-PB-vac, as shown in Figure 1. The shoulder at 708.1 eV and the peak at 708.5 eV are attributed to $Fe(2p_{3/2}) \rightarrow Fe(3d, t_{2g})$ and $Fe(2p_{3/2}) \rightarrow Fe(3d, e_g)$ transitions, respectively. The peak at 710.4 eV corresponds to $Fe(2p_{3/2}) \rightarrow \pi^*$, and the peak at 712.6 eV corresponds to $Fe(2p_{3/2}) \rightarrow \sigma^*$ transitions [1]. The peaks at 720.5 and 721.5 eV are assigned to $Fe(2p_{1/2}) \rightarrow Fe(3d, t_{2g})$ and $Fe(3d, e_g)$ transitions, respectively. We observed a slight shift of the signals ($L_{2,3}$ edges) towards lower energy values in Ni-PB-vac, suggesting the replacement of cyanide ligands with water ligands. For Ni-PB, the Ni L_3 edges show a shoulder at 853.5 eV, a peak at 855.5 eV, and a peak at 859.8 eV, which are assigned to $Fe(2p_{3/2}) \rightarrow Fe(3d, e_g)$ with a change of symmetry ($O_h \rightarrow C_{4V}$), $Fe(2p_{3/2}) \rightarrow Fe(3d, e_g)$, and a satellite peak, respectively. We observed good stability after the catalytic test. Further experiments are required to fully understand the mechanisms of the reaction.

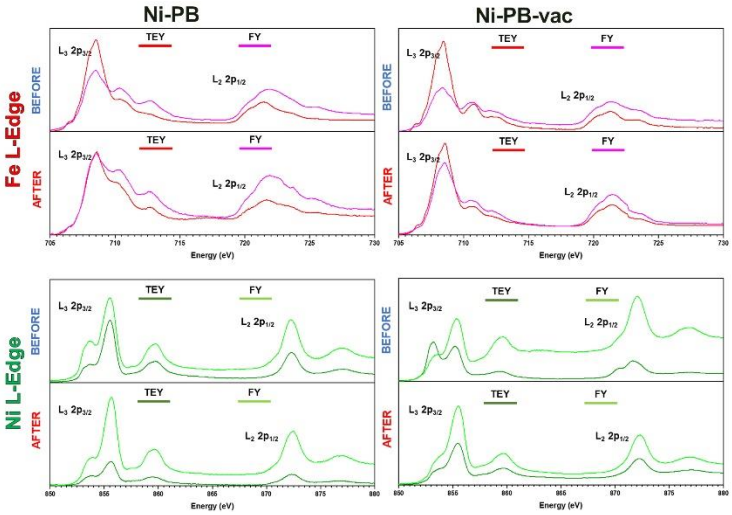

Figure 1. Soft x-ray absorption spectra for Fe and Ni $L_{2,3}$ edges in Ni-PB and Ni-PB-vac. Total Electron Yield (TEY) → surface of the catalyst and Fluorescent yield (FY) → bulk analysis.

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References

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