Analysing *operando* Mössbauer spectra of battery materials: a chemometric approach to the study of NaFeO$_2$ as positive electrode material for Na-ion batteries

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Among the possible positive electrode materials for Na-ion batteries, iron-based oxides have been regarded as promising solids for the reversible insertion/deinsertion of Na on the basis of their abundance in the Earth's crust. In particular, O3-type NaFeO$_2$, easily prepared from the reaction of iron oxide and Na$_2$CO$_3$ at 600°C, has been identified as the most interesting one from the viewpoint of both gravimetric and volumetric energy density.[1–3] Na/NaFeO$_2$ cells cycle through a relatively flat potential plateau between 3.3 and 3.4 V vs. Na$^+$/Na, commonly associated with the Fe^{4+}/Fe^{3+} redox couple. However, if cycling is extended above 3.5 V, other irreversible reaction plateaux appear, which completely inactivate the material. ^{57}Fe Mössbauer spectroscopy is thus a method of choice for the study of both (1) the cycling mechanism and (2) the irreversible reactions occurring above 3.5 V.

In this work, *operando* ^{57}Fe Mössbauer spectra were collected during the electrochemical cycling of NaFeO$_2$ vs. Na metal using a specifically designed in situ cell,[4] and analysed using an alternative and innovating data analysis approach based on chemometric tools such as Principal Component Analysis (PCA) and multivariate curve resolution (MCR).[5,6] This approach, which allows the unbiased extraction of all possible information from the *operando* data, enabled the stepwise reconstruction of the "real" spectral components occurring during the cycling of NaFeO$_2$. In this way, a clear description of the electrochemically active iron species could be obtained, allowing a clearer comprehension of the cycling mechanisms of this material vs. sodium.

Références :
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