How reliable is the Na metal as a reference electrode?

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There is no doubt that Li-ion batteries are nearing their limitations in terms of energy density, lifetime and safety, and the progress is slower than expected. Thus, other alkali metals, especially Na, are currently being extensively investigated as alternatives to Li metal. So far, electrochemical systems based on Na-ion have been mostly considered to be purely academic. This system has been considered to be purely academic, and no real applications have been developed to investigate its viability, the only exception being the high temperature Na-S system, which was commercialized in the 1960s. Recently, however, the amount of research and the number of papers devoted to the development of active materials for Na-ion batteries is exponentially increasing, reflecting the interest of the battery community to re-consider the commercialization of Na-ion batteries in the near future.
To date, most of the studies of novel materials for Na-ion batteries are performed using Na metal as both counter and reference electrode. Knowing the increased reactivity and sensitivity of the Na compared to Li metal, the question has been raised whether Na metal is a reliable reference electrode. In an attempt to answer it, by means of electrochemical impedance spectroscopy, EIS, we were studying the interfacial reactions taking place at the surface of the Na metal. We employed symmetric Na/Na cells and at first focused on the impact of the presence of a native oxide layer on the surface of Na 1. As can be seen in Figure 1, scratching of the surface of the Na metal is crucial for improving the electrode/electrolyte interphases and, thus, ensuring reproducible results. In addition, other parameters, such as the thickness of the Na metal foil, the presence of air and water in the electrolyte, and electrolyte additive have a strong impact on the impedance response of the symmetric Na/Na cell. Although the results are still being analyzed, the knowledge acquired from these experiments has already resulted in modified cycling protocol and an example of the Na-ion cell with the optimized Na metal counter electrode will be presented.

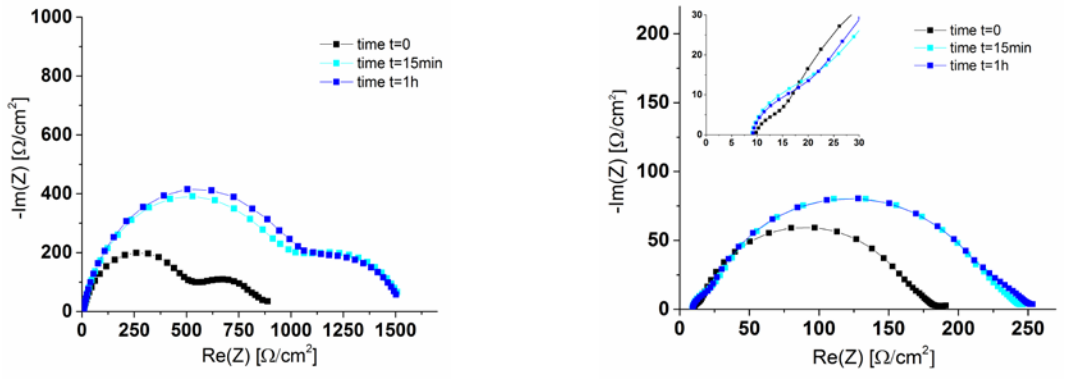

Fig.1. Representative EIS spectra of symmetric Na/Na cells assembled with (left) the non-scratched and (right) the scratched Na metal electrodes.

References:
[1] Conder J., Villevieille C., Journal of Power Sources, 2018, Submitted