

High surface nickel-based air electrode for rechargeable alkaline metal-air batteries

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Alkaline metal-air batteries have become subject of intensive research since they offer very high volumetric and gravimetric energy densities [1] [2]. In order to make such batteries rechargeable, the air electrode must be able to work bidirectionally to enable charging and discharging of the system. Hence it must contain a suitable catalyst, which facilitates both reactions, oxygen-evolution-reaction (OER, charging-reaction) and oxygen-reduction-reaction (ORR, discharging-reaction). Suitable catalysts for these two reactions are precious metals like Pt [3]. But due to their high costs precious metals cannot be used in commercial batteries. In order to avoid these expensive metals, research has especially focused on catalysts, which are based on rare-earth metals [4]. However, in comparison to precious metals their catalytic activity for the OER is low leading to a poor charging performance. Therefore, we developed a new type high surface nickel-based air electrode, which avoids these drawbacks by using one catalyst for each reaction.

In this system the OER is induced by nickel as NiO(OH) arises inherently at the interface between nickel and the alkaline electrolyte under charging-conditions. The formed NiO(OH) layer in turn acts catalytically for the OER [5]. When using the air electrode in discharging-direction the NiO(OH) gets reduced, due to the fact that the equilibrium-potentials of the reversible NiO(OH)-formation ($\varphi_{00, Ni^{2+}/Ni^{3+}} = 0,490$ V vs. NHE @ pH 14) and the equilibrium-potential of the OER ($\varphi_{00, O_2/OH^-} = 0,404$ V vs. NHE @ pH 14) are nearly identical. By this, surface-NiO(OH) is formed each time anew, when the electrode is operated under the charging-conditions. This catalytic effect strongly depends on the nickel-surface-area and thus can be increased by the use of highly porous nickel-foam or nickel-powder. For the ORR it is possible to revert to non-noble catalyst-materials, which are established from monodirectional air electrodes of metal-air batteries, such as carbon black (C) or manganese-dioxide (MnO₂). [6].

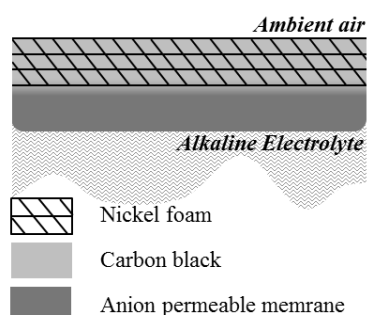


Figure 1: Schematic design of a high surface nickel-based air electrode

To proof the working-principle of this concept, a simple high surface nickel-based air electrode (see Fig. 1) was built up, consisting of three components: Nickel foam was chosen, to induce the OER and to serve as mechanical frame. A layer of C inside the nickel foam acts as the catalyst for the ORR. An anion-permeable

membrane (AEM), based on a quaternary ammonium-group, acts as binder for the C, seals against leakage of electrolyte and avoids intoxication by carbonate-formation. For comparison also high surface nickel-based air-electrodes without C have been manufactured.

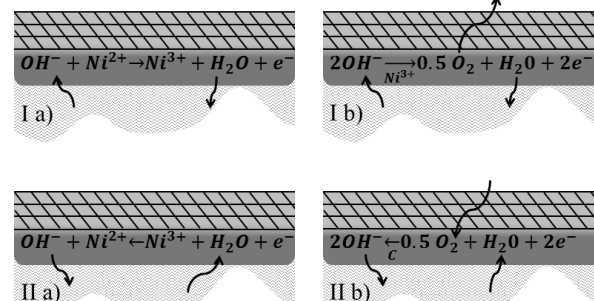


Figure 2: Working-principle of the nickel-based air electrode: I) charging-mode: a) NiO(OH)-formation, b) oxygen-evolution; II) discharging-mode: a) NiO(OH)-reduction, b) oxygen-reduction

The functionalities of the electrodes have been verified by cyclic voltammetry (CV). As can be seen in Figure 3 the air electrode works in both charging and discharging direction. In contrast, a commercial air electrode can only induce the ORR (discharging) and the nickel air-electrode without C only supports the OER. It has been shown that the high surface nickel-based air electrode combines both catalytic mechanisms to enable bidirectional functionality and can be considered as a candidate for rechargeable alkaline metal-air batteries.

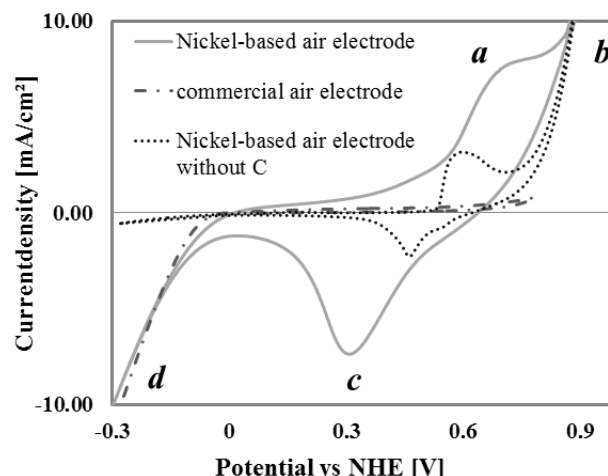


Figure 3: Cyclo-voltammetric plots of a nickel-based air electrode, a nickel-based air electrode without carbon and a mono-directional air electrode, with KOH-electrolyte (pH 14). The characteristic points refer to: *a*) NiO(OH)-formation, *b*) OER, *c*) NiO(OH)-reduction, *d*) ORR.

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