Sustainable Energy & Fuels

Accepted Manuscript

Volume 1 | Number 1 | 2017 | Pages 1–100

Sustainable Energy & Fuels

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Poly(ionic liquid) Binders as Ion conductors and Polymer Electrolyte Interface for Enhanced Electrochemical Performance of Water Splitting Electrodes

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Abstract

A poly(ionic liquid) (PIL) was used as a binder for NiCo oxide nanopowders in a water electrolysis standard assay to explore the role of polymers in a model electrocatalytical device. The comparison to technical standard binders such as Nafion™ or Fumion™ ionomer, showed that the PIL improves the cycling stability under accelerated ageing conditions as well as the activity.

Electrochemical energy storage and conversion processes are attracting tremendous attention due to their active role in utilizing the fluctuating sources of sustainable energy.[1] New electrode materials and – potentially- stable solvents and electrolytes have to be developed to survive harsh conditions in electrolysers, fuel cells, and batteries. Interestingly, the binder, needed for the engineering of powder catalysts, is hardly considered to be object of improvement. Such binder material accounts for typically 10wt% of the electrode mass and effectively "glues" all powderous components, such as electrochemically active species and conductive additives, into a mechanically stable electrode to endure the operation conditions.[2] A few groundbreaking primary studies[3-9] have shown that the significant effects of polymer binders on the overall performance of many electrochemical devices can be expected, particularly with respect to the resulting mechanical properties and interactions with electrolytes and active material. Poly(vinylidene fluoride) (PVDF) is a standard choice for organic electrodes in lithium ion batteries, but even for PVDF the lifetime is restricted, as for instance proven by the increase in contact resistance throughout longer operational runs or even just by the detection of degradation products within the devices. [10] For aqueous systems, purely hydrophobic systems have to be avoided, and a standard choice is for instance Nafion™-based binder[11]. From a chemical perspective, Nafion is a well-known ion and water conductive membrane material, but it is not designed to survive both the harsh reductive as well as oxidative conditions in modern electrodes, as it will be also shown below. We believe next-generation binders must be able to participate in the main electrochemical reactions, and be significantly more robust and conductive than the state-of-the-art to solve the issues plaguing current systems. Ionic liquids (ILs) are used in several electrochemical energy storage/conversion devices due to their favorable physical properties such as negligible vapor pressure, high ion conductivity, chemical inertness and most importantly, a broad electrochemical window.[12-18] Recently, the favorable application profile was extended to poly(ionic liquid)s (PILs), which combine IL with polymer characters.[19-21] PIL copolymers have already been examined as binders for electrodes of lithium-batteries and showed indeed superior

performance.[22] When applied as binders in cathodes of lithium ion batteries, vinylimidazolium-based nanoparticle binder offered not only a higher specific capacity compared to PVDF but also an outstanding long-term electrochemical durability at least for 1000 charge–discharge cycles.[23] These primary experiments, though elucidating great potential of PIL as binders in electrochemical devices, were, however, still performed in organic solvents and at rather moderate oxidation potentials. In order to design a PIL with binding function, they generally must satisfy certain requirements. First, the binder must be sufficiently insoluble in the electrolyte to prevent dissolution of the PIL and loss of binding function. Additionally, the PIL should swell within the electrolyte to help facilitate ion transport and retain some activity of the bound components and finally the PIL should be resistant to the operating conditions, or react to form a product that is resistant to degradation. The PIL chosen here satisfies these requirements and is easily synthesized on the tens of grams scale. Herein, we extend this work to much higher oxidation potentials and corrosive alkaline aqueous conditions with oxygen in status-nascendi, as they are for instance found in water electrolysis. We use a PIL binder to fabricate a powdery NiCo mixed oxide electrode and compare it with two commercial standard binders and a blank sample without binder. Not only good performance and high stability could be proven, but the compound system even surpassed the performance of the pure electrocatalyst as such. PILs are a class of functional polymers featuring a high density of IL species, *i.e.* one per monomer unit, as well as a multivalent binding power *via* covalent connection of IL species into a polymer backbone. The interest in applying PILs as binder materials in electrochemical devices relies on their broad electrochemical window endorsed by the electrochemically stable IL moieties and enhanced surface activity, two of the key criteria in designing binder materials. The chemical structure of the PIL binder tested in this study is shown in **Figure 1**. The PIL is imidazolium-based, with the imidazolium cation attached directly to the polyvinylene backbone and was prepared via conventional free radical polymerization of an ionic liquid monomer 1-ethyl-3-vinylimidazolium bromide, followed by an anion exchange reaction of the polymer to replace Br$^-$ with an electrochemically inert anion, bis(trifluoromethane sulfonyl)imide (TFSI). While the as-synthesized PIL would normally contain a bromide counter anion, we chose TFSI to reduce solubility of the PIL in the electrolyte. Tetrafluorobrate and hexafluorophosphate anions are potential candidates to reduce PIL solubility, however they are known to undergo hydrolysis and were not examined[24]. Titration test using a AgNO$_3$ solution proves the quantitative anion exchange process.
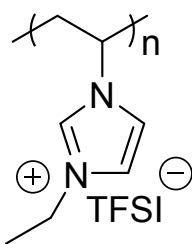
PIL-1

Figure 1. Chemical structure of the PIL binder tested in this study.

The chemical structure of the polymer was characterized and proven by nuclear magnetic resonance spectroscopy (Fig. S1). The molecular weight of this polymer was characterized to be 130 kDa by gel permeation chromatography. The activity and stability properties of a commercial NiCoO$_2$ mixed oxide catalyst, adhered on a glassy carbon support with PIL, Nafion and Fumion binders and no binder, were investigated by means of linear sweep voltammetry and chronopotentiometry, respectively. All measurements were conducted in an electrochemical flow

cell, described elsewhere[25] in 1M KOH, with internal resistance (IR)-correction (see SI). All stability and activity measurements, in this work, have been performed under chronopotentiometric mode, by applying constant 10mA/cm^2 for 2h and by linear sweep voltammetry at 1.2-1.7V$_{RHE}$. For the entirety of catalysts electrochemical characterization a flow rate of 0.86ml/min was used, because it provides a good balance between oxygen gas removal from the catalyst surface and sufficient detection, from the ICP-OES, of the catalyst corrosion products. Lower flow rates are unable to provide reproducible experimental conditions due to excessive oxygen bubble formation at such high current densities. The catalyst used in this work was a commercial NiCoO$_2$ mixed oxide (Sigma Aldrich, 99% metal basis, >150nm particle size). The catalysts reach their operation state, in which all activity and stability measurements are performed in this work, after a preconditioning step by means of cyclic voltammetry between 1.0-1.45V$_{RHE}$ at a scan rate of 100mV/s for 250 cycles (Fig. 2).
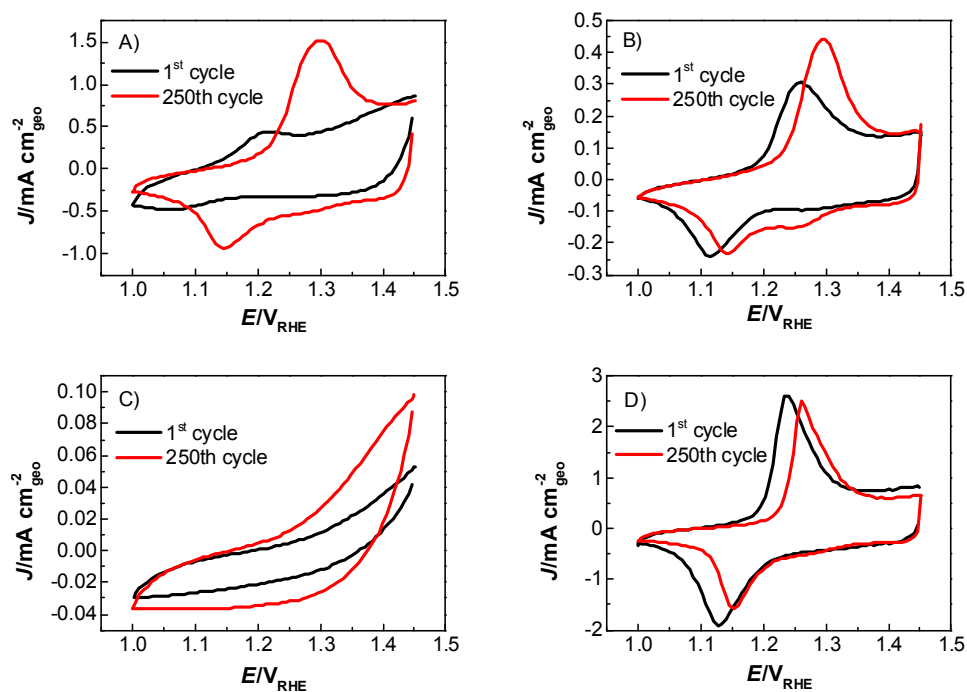

Figure 2. Cyclic voltammetry between 1.0-1.45V$_{RHE}$ at a scan rate of 100mV/s of a mixed NiCoO$_2$ oxide powder catalyst using different binders in 1M KOH. Significant potential shifts are observed for all catalysts which is evidence of surface ordering. (A-B) PIL-1 and Nafion have similar a potential profile indicating that after potential cycling the catalyst surface remains protected by the binder. (C) The Fumion covered sample is completely inactive due to severe surface coverage by the binder which significantly blocks active sites. D) The No-binder system shows only a potential shift.

Catalyst activity characterization was performed by means of linear sweep voltammetry between 1.2-1.7V$_{RHE}$ at a scan rate of 5mV/s before and after a stability test at chronopotentiometric mode at a current density of 10mA/cm^2 for 2h. Activity gain is observed before and after the preconditioning step. As a result, catalyst preactivation is necessary for the catalyst to reach its final state. Thereafter, linear sweep voltammetry between 1.2-1.7V$_{RHE}$ was applied for a second time on every catalyst to evaluate a comparable catalyst activity (Fig. 3). The catalyst stability was tested using chronopotentiometry at 10 mA/cm^2 for 2 h (Fig. 4) with simultaneous transient analysis of the corrosion products using an ICP-OES connected on the outlet of the electrochemical flow cell (Fig. 5). After the stability evaluation measurements linear sweep voltammetry was used for comparison of the initial and final activity of the catalysts investigated.

Neither Glassy carbon nor the pure PIL binder showed any detectable electrocatalytic water splitting activity as such. NiCo oxide as a bare powder electrode as well as Nafion reveled the same voltage-current-curve, speaking for practically resistant-free gluing of the particles. Initially, the PIL binder showed a curve which is shifted to higher potentials by ca 25 mV.
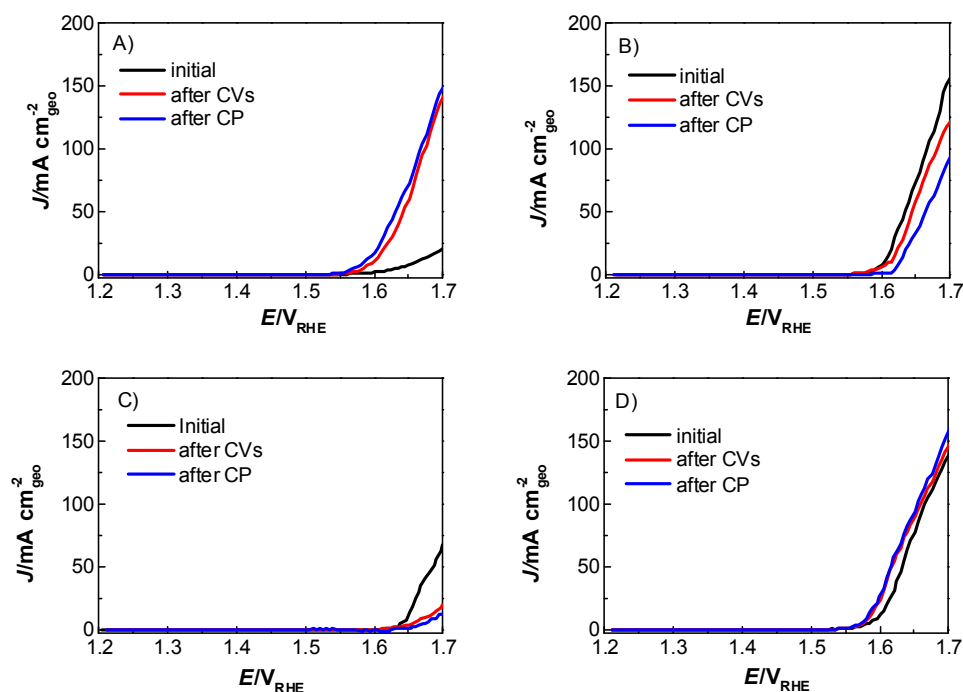

Figure 3. Linear sweep voltamograms from 1.2-1.7V_{RHE} of A) PIL-1, B) Nafion, C) Fumion and D) no binder, of a commercial mixed oxide $NiCoO_2$ catalyst with a sweep rate of 5mV/s, in 1M KOH.

This effect is attributed to a minor amount of added resistance which is more pronounced for Fumion. The catalyst prepared with Nafion presented the highest initial activity from all catalysts. However, upon catalyst preactivation, by cyclic voltammetry, the activity decreased and went down even further after the actual stability test. Similarly, a decrease of the catalytic activity was also observed for the catalyst prepared with Fumion and the binder-free catalyst. On the contrary, the catalyst prepared with the PIL-1 binder was significantly activated after the cyclic voltammetry activation step and surprisingly the activity further increased even after the 2h chronopotentiometric stability investigation (Fig. 3a).This can be attributed to the fast removal of oxygen bubbles from the catalyst surface during the stability tests at a flow rate of 0.86 ml/min due to the hydrophilic nature of the PIL-1 polymer binder. Fast oxygen bubble accumulation on the catalyst surface reduces the available catalytic surface which results in fluctuating potential rise observed as spikes recorded in the potential profiles of each catalyst (Fig. 4). Potential spikes not only have a detrimental effect on the catalyst stability but also on the activity. In the case of Fumion the activity was very low ($E_{J=10mAcm^2}$= ~2.0V_{RHE}), and the potential during stability measurements was not stable due to inadequate surface oxygen removal. Here, within the first 25 min the oxygen evolution overpotential increased by more than 100mV. ICP-OES corrosion profiles follow closely the chrono-potentiometric ones where it could be observed that the potential spikes on the stability measurements and the Ni and Co ICP spikes on the ICP-OES measurements follow a similar pattern due to the higher metal corrosion at higher potential values.
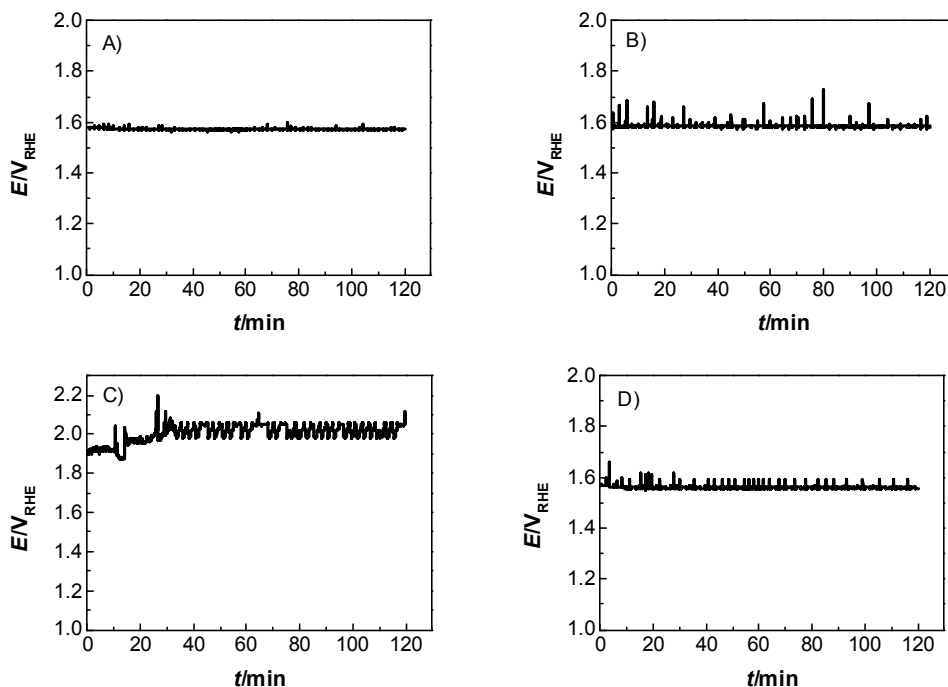
Figure 4. Chronopotentiometric analysis of catalyst stability at j = 10 mA/cm^2 for 2h of A) PIL-1, B) Nafion, C) Fumion and D) no binder, of a commercial mixed oxide $NiCoO_2$ catalyst in 1M KOH. The catalyst with Fumion binder shows rather rapid degradation, while the PIL binder not only slightly increases, but even outperforms the pure catalyst powder.

It is known that PILs tend to spread and stick to surfaces of metals[26-28] and some metal-oxides[29], i.e. they try to cover a surface/ curved surface with a homogenous film of about 2- 5 nm thickness, which also contains solvating water.[30,31] This layer acts as a local membrane, protecting and gluing the catalyst particles, while being permeable for water and anions via dynamic counterion exchange. This indicates that the PIL favorably interacts and spreads on the catalyst surface, as opposed to agglomeration which is more typical of an incompatibility.　Note that the PIL is a polycation being permeable preliminarily for anions. Unlike some perfluorinated binders, the PIL can swell in the electrolyte and still allows for activity of the underlying catalyst. Assuming a particle size of 100 nm for the electrocatalyst, we can calculate a stoichiometric layer thickness of ca 5 nm, i.e. there is enough binder available for such type of distribution. IR-spectroscopy measurements of the catalyst before and after electrochemical measurements revealed that the vibrations corresponding to the PIL remains at ~700 cm^{-1}, ~1200 cm^{-1} and at ~1400 cm^{-1}, indicating that the polymer is neither decomposing nor dissolving under experimental conditions. SEM images (Fig. S3) further prove the existence of the PIL binder before and after the electrochemical stress test at 10mA/cm^2. The fact that the chronoamperometry indicates even an improvement of the electrocatalyst shows at the optimal layer formation and structuration is reached only after 30 minutes in operation, i.e. active SEI formation is a slow process. Destruction of this structure is not occurring under the conditions of this test, for this, we obviously have to move to still higher overpotentials.
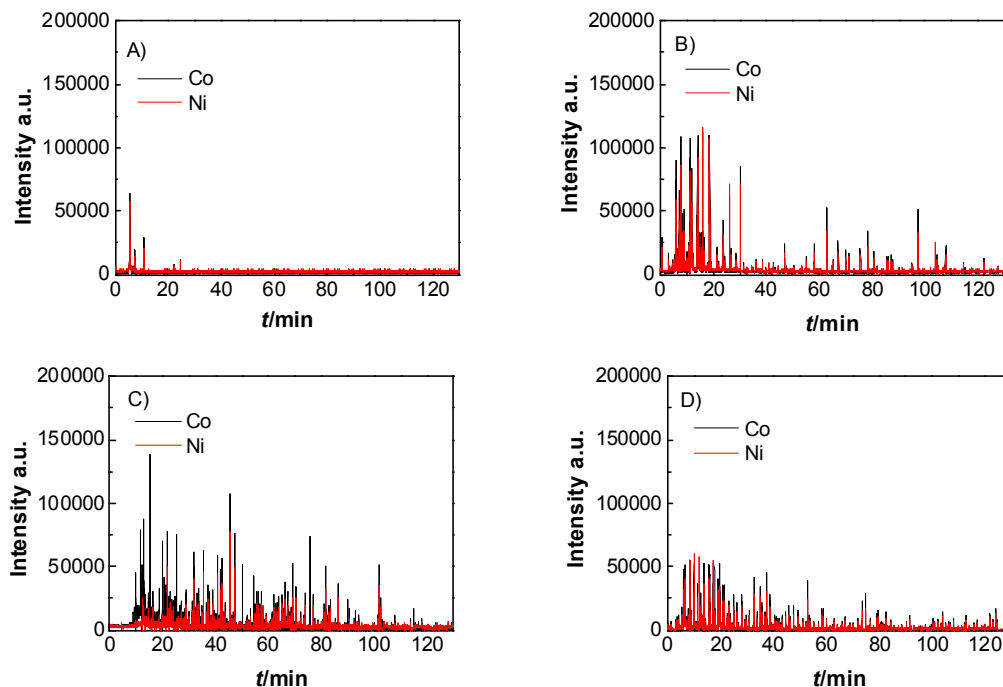
Figure 5. ICP-OES transient profiles of A) PIL-1, B) Nafion, C) Fumion and D) no binder, of a commercial mixed oxide NiCoO$_2$ in 1M KOH. Corrosion profiles of each catalyst used reveals a significantly better stability for the PIL-1 supported catalyst due to fast oxygen bubble removal from the catalyst surface.

Worth mentioning is that the PIL binder outperforms all other systems in peak performance, i.e. the local membrane structure is at all not rate-limiting the catalytic processes. The whole model is illustrated in Fig. 6.
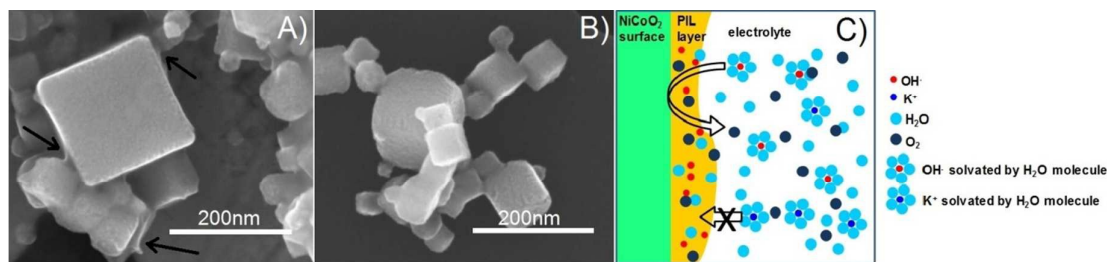

Figure 6. A) PIL covered NiCoO2 nanoparticles (arrows in black point at the edges of nanoparticles where the PIL is covering the catalyst), B) PIL-free Nanoparticles and C) Schematic illustration of the PEI. The PIL blocks metals at the electrode, while it is permeable for water, hydroxy-ions and the as generated oxygen, with bubbles nucleating outside of the PEI layer.

In conclusion, we show that a polymeric ionic liquid can be used as a binder to formulate nanoparticulate water oxidation catalysts and create a highly active and stable electrode. When compared to two commercial binders, the PIL shows higher oxidation stability and a better lifetime behavior. The addition of binder even improves the stability of the electrocatalysts such, which we attribute the formation of a polymeric solid electrolyte interface layer (PEI), very similar to the solid electrolyte interface layer known from operational batteries, but here not formed in situ but a-priori added. A more realistic stability testing will of course have to include significantly higher overpotentials, potentially other reactions and catalysts. On the other hand, it is still possible to improve the PIL structure to implement even higher oxidation stabilities, and the

related HOMO levels of appropriate organic compounds (to secure thermodynamic stability) can be as positive as + 3 V. We believe that the use of functional binders with adjusted swelling, dielectric environment, and ion permeation behavior is a new strategy to impact electrocatalysis and electrochemical heterophase reactions in general, enabling potentially a better rate behavior, but essentially a higher selectivity and longer lifetimes of the resulting overall systems.

Acknowlededments

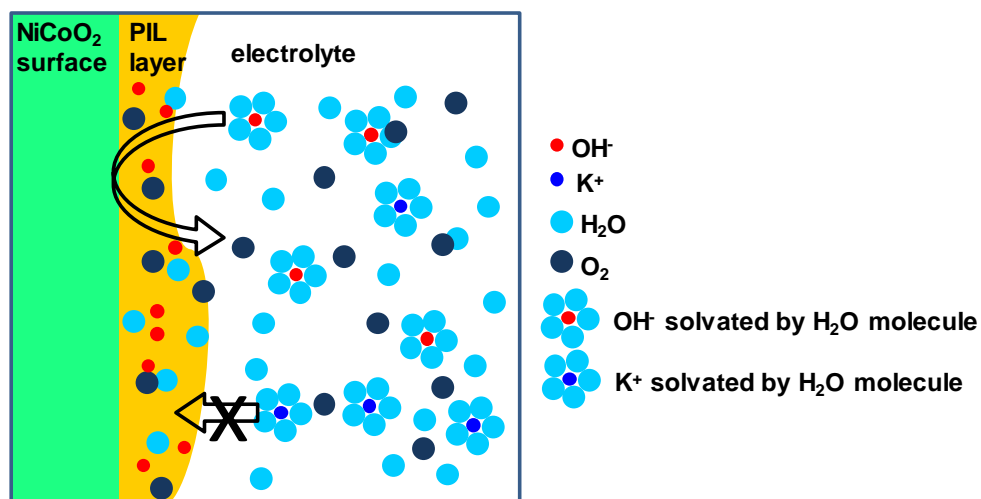## References

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