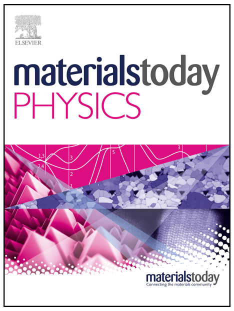

Systematic study of the influence of iR compensation on water electrolysis

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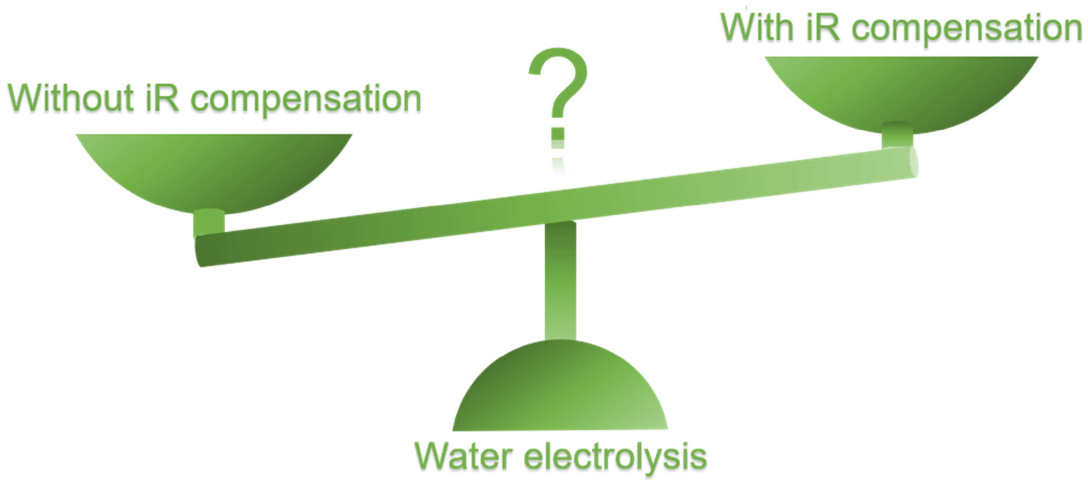
Z. F. R. led the project. L. Y. designed and performed the experiments and analyzed the data. Z. F. R. and L. Y. discussed the results and wrote the paper together.


Without iR compensation
?
With iR compensation
Water electrolysis

Systematic study of the influence of iR compensation on water electrolysis

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Abstract

Water electrolysis has been one of the most studied topics in materials research in the past decade because of the global effort in exploring clean and renewable energy sources. Much effort has been devoted to developing highly active electrocatalysts for the two half reactions of water electrolysis, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Some reported electrocatalysts are even superior to the benchmark platinum and iridium dioxide catalysts, and thus are claimed to be promising for large-scale commercial use. However, most electrochemical data in the literature are reported after iR compensation, where R is the overall resistance, including contact resistance, charge-transfer resistance, and intrinsic resistance. Unfortunately, these types of resistance cannot be avoided in real electrolyzers, which means that R still results in energy consumption if the electrocatalysts are used for industrial water electrolysis. Thus, the data with iR compensation is always misleading, and setting criteria for iR compensation in analyses of water electrolysis is urgently needed to instruct the scientific community. In this work, we test the catalytic performance of several reported HER and OER catalysts with and without iR compensation and discuss the contribution from iR compensation under small and large current densities. We also present a comparative study between two iR-compensation methods (automatic and manual iR compensation). Finally, we propose some strategies to reduce the R in order to achieve better performance without iR compensation, which is necessary for industrial applications.

Keywords: Water electrolysis; HER; OER; iR compensation

1. Introduction

Electrochemical water splitting, also known as water electrolysis, is a green and efficient technology for large-scale hydrogen production, and has been one of the most studied topics in materials research in the past decade because of the global effort in exploring clean and renewable energy sources [1-3]. In general, water electrolysis consists of two half reactions, *i.e.*, the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER) [4-7]. The two-electron transfer of HER and the four-electron-proton coupled process of OER result in large energy barriers, significantly slowing down the water electrolysis kinetics and leading to the requirement of an input potential much larger than the thermodynamic potential of 1.23 V [8,9]. Although the noble-metal catalysts of platinum (Pt) and iridium dioxide (IrO_2) exhibit benchmark activity for HER and OER, respectively, the scarce reserves and high cost of these materials severely hamper their large-scale application [10-12]. Therefore, great effort has been devoted to developing highly active electrocatalysts based on non-noble-metal materials to replace these noble-metal catalysts.

Remarkable progress has been made in developing non-precious water-splitting electrocatalysts, including carbon-based materials [13-15], transition-metal oxides [16], (oxy)hydroxides [17], sulfides [18], selenides [19], carbides [20], nitrides [21], borides [22], phosphides [23,24], phosphates [25], layered double hydroxides (LDHs) [26], alloys [27] *etc.* Benefiting from a high density of active sites and good intrinsic activity, some of the HER candidates (*e.g.*, Mo_6Ni_6C [28] in acidic solution and $MoNi_4$ [29] and NiMoN [30] in basic solution) show excellent HER activity approaching or even superior to that of the benchmark Pt, while a majority of OER catalysts exhibit better performance than the benchmark IrO_2 in alkaline electrolyte. These efficient catalysts can deliver large current densities at very small overpotentials, and thus are claimed to be promising for large-scale commercial use. Nevertheless, almost all of the overpotential data in the literature are reported with iR compensation, where R is the overall resistance, including contact resistance between the catalyst and the substrate, charge-transfer resistance between the catalyst and the electrolyte, and intrinsic resistance of the catalyst, and i is the current at a particular current density. Equations (1) and (2) describe iR compensation for HER and OER, respectively:

$$\eta_{\mathrm{HER}} = E_{\mathrm{RHE}} - 0\ \mathrm{V} - E_{\mathrm{iR}}, \tag{1}$$

$$\eta_{\mathrm{OER}} = E_{\mathrm{RHE}} - 1.23\ \mathrm{V} - E_{\mathrm{iR}}, \tag{2}$$

where η_{HER} and η_{OER} represent the overpotential for HER and OER, respectively, at a particular current density; E_{RHE} is the measured potential *vs.* reversible hydrogen electrode (RHE); and E_{iR} is the iR-compensated overpotential. The reason to conduct iR compensation when obtaining polarization curves is to show the inherent catalytic activity of an electrocatalyst. Unfortunately, contact resistance, charge-transfer resistance, and intrinsic resistance cannot be avoided in a real electrolyzer, which means that R still results in electrical energy consumption if the electrocatalyst is used for industrial water electrolysis. From this point of view, overpotential determined without iR compensation is more meaningful than that with iR compensation, especially when the difference between the two is very large at a large current density. However, little attention has been paid to this issue thus far. Two years ago, Subrata Kundu's group discussed iR compensation in a perspective paper and appealed to researchers to provide the details of iR compensation methods used for their own reports [1]. To better instruct the scientific community, it is thus necessary to set criteria for iR compensation in analyses of water electrolysis. In this work, we synthesize some reported HER and OER electrocatalysts and test their catalytic performance with and without iR compensation. We then discuss the contribution of iR-compensated overpotentials under different current densities in detail. We also conduct a comparative study between two iR compensation methods: iR compensation set up by an electrochemical workstation automatically and manual iR compensation by calculation of series resistance. Finally, we propose some strategies to reduce the R in order to achieve better performance without iR compensation.

2. Results and discussion

For HER, we synthesized two efficient non-noble metal catalysts of $MoNi_4$ [29] and NiMoN [30] supported on Ni foam, as well as commercial Pt/C loaded on Ni foam as a benchmark electrode for comparison. Complete experimental details are provided in the Supporting Information. From the polarization curves shown in Fig. 1a, we can observe that both the NiMoN and $MoNi_4$ catalysts show excellent HER activity with iR compensation, and both are superior to Pt/C. Based on the overpotential summary in Table 1, the overpotentials with iR compensation are very small for the NiMoN and $MoNi_4$ catalysts. Even under large current densities of 500 and 1000 mA cm^{-2}, the overpotentials for NiMoN are only 125 and 167 mV, respectively, and 103 and 157 mV for $MoNi_4$ at the two respective current densities with iR compensation. In comparison, the required overpotentials at the same current densities for the Pt/C benchmark are 252 and 353 mV, respectively, with iR compensation. However, without iR compensation, the overpotential required by each of the three electrodes exhibits increases significantly, especially under large current densities. For the NiMoN catalyst, the overpotential at a small current density of 50 mA cm^{-2} increases from 43 mV (with iR compensation) to 61 mV (without iR compensation), and the overpotential at this current density likewise increases from 41 to 65 mV for $MoNi_4$ and from 52 to 60 mV for Pt/C. Under large current densities of 500 and 1000 mA cm^{-2}, the overpotentials without iR compensation are 376 and 713 mV, respectively, for NiMoN. For MoNi$_4$, the

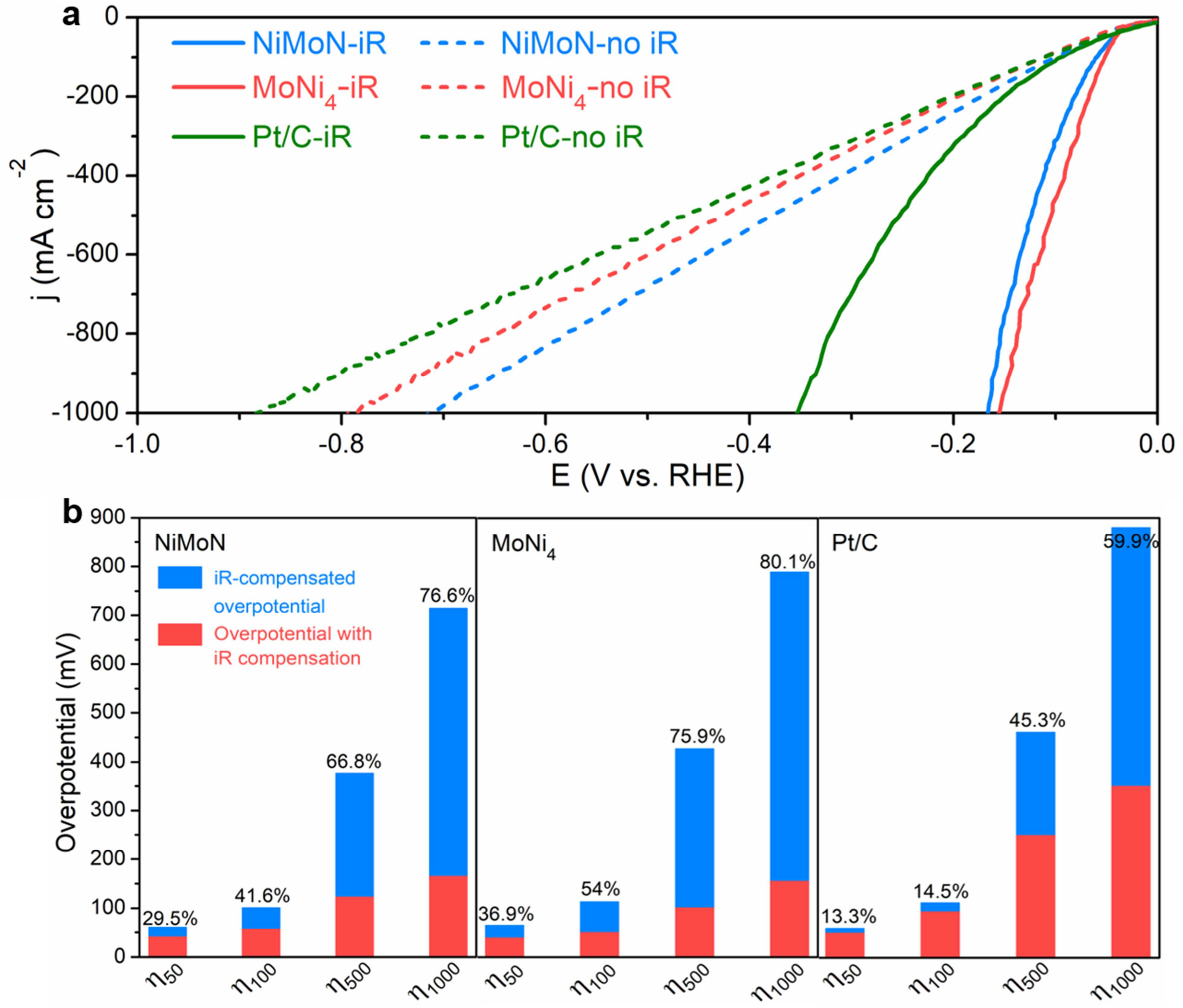

Fig. 1. HER performance in 1 M KOH. (a) Polarization curves of different catalysts with and without iR compensation. iR compensation was conducted automatically using a current-interrupt (CI) method. (b) Comparison of iR-compensated overpotential and overpotential with iR compensation among different catalysts. Here η_{50}, η_{100}, η_{500}, and η_{1000} represent the overpotentials at current densities of 50, 100, 500, and 1000 mA cm^{-2}, respectively. Each

percentage is the ratio of iR-compensated overpotential in the overpotential without iR compensation.

overpotentials even increase to 427 and 789 mV at the two respective large current densities. Interestingly, the HER activity of NiMoN is slightly worse than that of $MoNi_4$ with iR compensation, but without it, NiMoN is superior to $MoNi_4$. This reversal demonstrates that the NiMoN catalyst has a smaller overall resistance, so NiMoN may be a better candidate for industrial use compared to $MoNi_4$.

Table 1. HER overpotentials for different catalysts at different current densities with and without iR compensation.

Catalyst	iR compensation	η_{50} (mV)	η_{100} (mV)	η_{500} (mV)	η_{1000} (mV)
NiMoN	With	43	59	125	167
	Without	61	101	376	713
$MoNi_4$	With	41	52	103	157
	Without	65	113	427	789
Pt/C	With	52	96	252	353
	Without	60	112	461	880

To study the overpotential contributed by the iR compensation (iR-compensated overpotential, which is the overpotential difference between that with and without iR compensation), we calculated the ratio of iR-compensated overpotential in the overpotential without iR compensation. As shown in Fig. 1b, under a small current density of 50 mA cm^{-2}, this ratio is 29.5% and 36.9% for NiMoN and $MoNi_4$, respectively. When the current density reaches 100 mA cm^{-2}, the ratio increases to 41.6% and 54% for NiMoN and $MoNi_4$, respectively. Under the industrially required current densities of 500 and 1000 mA cm^{-2}, the ratio is as high as 66.8% and 76.6%, respectively, for the NiMoN catalyst. This ratio is even larger for the $MoNi_4$ catalyst, 75.9% and 80.1% at the large current densities of 500 and 1000 mA cm^{-2}, respectively, indicating that the iR-compensated overpotential accounts for most of the real overpotential (overpotential without iR compensation). Very similar results were also demonstrated for a typical transition-metal chalcogenide catalyst, MoS_2 (Fig. S1). Therefore, the overpotential with iR compensation is always misleading, especially under large current densities. For the benchmark Pt/C catalyst, the ratio of iR-compensated overpotential is smaller than for the other two catalysts, which is due to the larger real overpotentials.

For OER, we synthesized two representative catalysts of NiFe LDH and NiFeN on Ni foam, along with the benchmark commercial IrO_2 loaded on Ni foam. Very similar to the results found for the HER catalysts, we can obtain the following results from the data shown in Fig. 2 and Table 2:

(1) The NiFe LDH and NiFeN catalysts exhibit better OER performance than that of IrO_2 both with and without iR compensation.

(2) There is an activity reversal under large current densities for the NiFe LDH and NiFeN catalysts without iR compensation.

(3) The difference between the overpotential with iR compensation and that without iR compensation is large when the current density is larger than 50 mA cm^{-2} (this was further confirmed by analyzing a typical transition-metal phosphide catalyst, NiFeP, as shown in Fig. S2).

(4) The overpotential without iR compensation is a more reliable reference for industrial application.

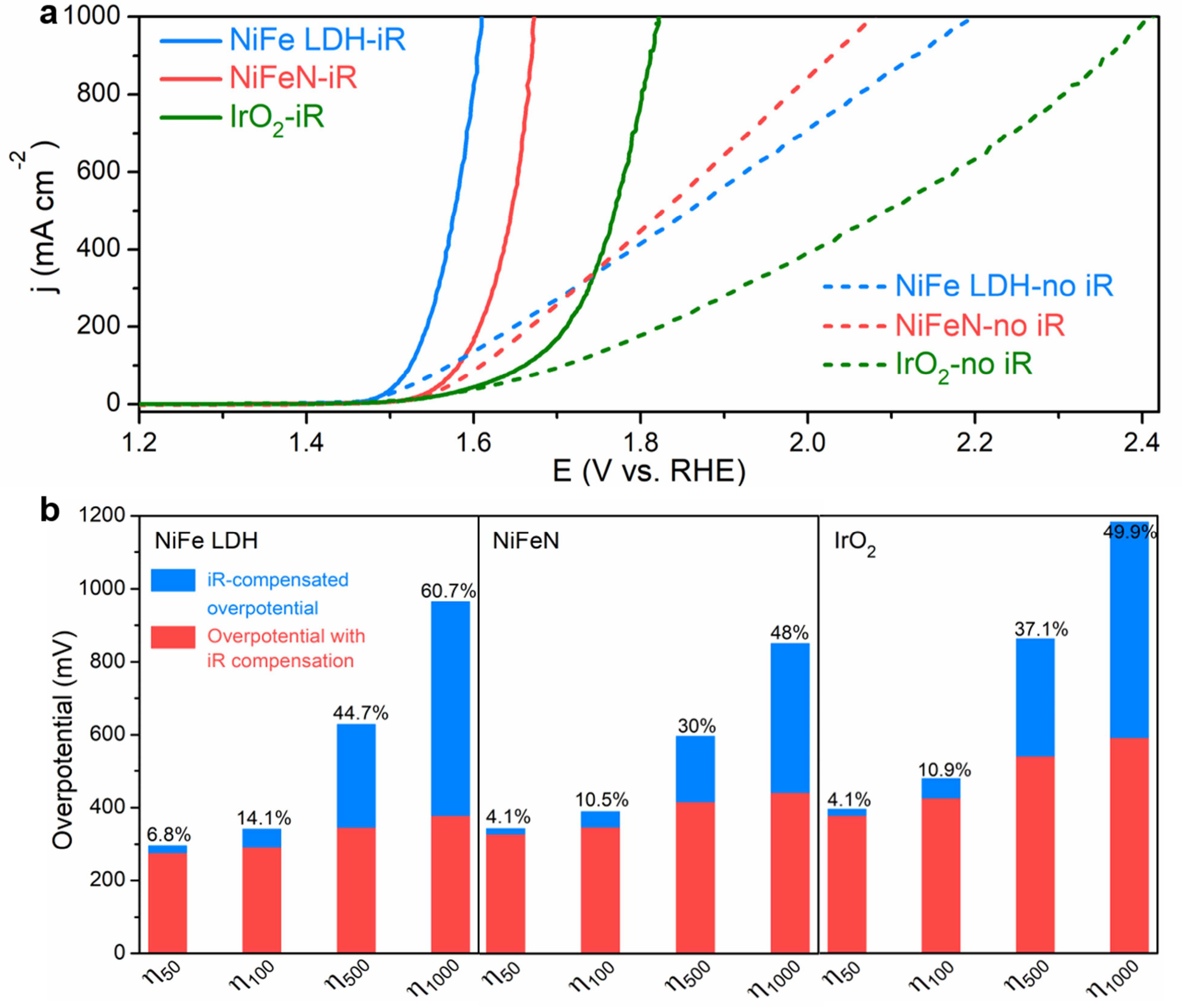

Fig. 2. OER performance in 1 M KOH. (a) Polarization curves of different catalysts with and without iR compensation. iR compensation was conducted automatically using a CI method. (b) Comparison of iR-compensated overpotential and overpotential with iR compensation among different catalysts. Each percentage is the ratio of iR-compensated overpotential in the overpotential without iR compensation.

Table 2. OER overpotentials for different catalysts at different current densities with and without iR compensation.

Catalyst	iR compensation	η_{50} (mV)	η_{100} (mV)	η_{500} (mV)	η_{1000} (mV)
NiFe LDH	With	276	293	347	379
	Without	296	341	628	965
NiFeN	With	329	348	417	442
	Without	343	389	596	850
IrO_2	With	379	426	542	592
	Without	395	478	862	1182

The iR compensation for the different HER and OER catalysts was conducted automatically using a CI method during testing on an electrochemical workstation. Another method that can be used to conduct iR compensation is manually calculating the series resistance (R_s) from electrochemical impedance spectroscopy (EIS) Nyquist plots. To compare the influence on the final results between these two methods, we also performed EIS for the HER and OER catalysts. To obtain the Nyquist plots shown in Fig. S3, we fit the data to a simplified Randles circuit, as shown in Fig. S4, and then used the calculated R_s values to determine 100% iR compensation manually. Based on the polarization curves shown in Figs. 3a and 3b, we can come to the same conclusion as with the CI method of iR compensation that the difference between the overpotential with iR compensation and that without iR compensation for either HER or OER is very large when the current density is larger than 50 mA cm^{-2}. From the overpotentials listed in Tables S1 and S2, we can see that those with manual iR compensation by the EIS method are very close to those with automatic iR compensation by the CI method at small current densities (50 and

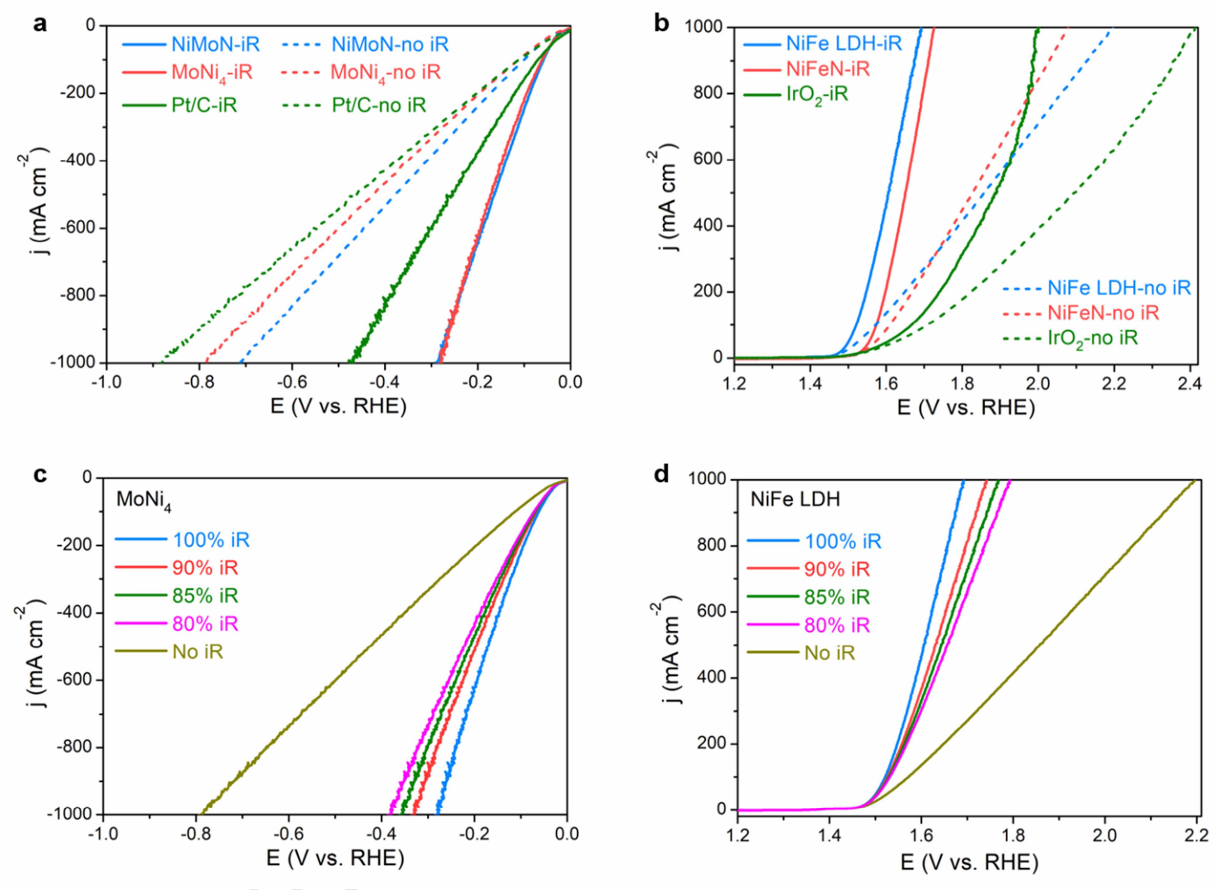

Fig. 3. (a) HER and (b) OER polarization curves of different catalysts with and without iR compensation. (c) HER polarization curves of $MoNi_4$ and (d) OER polarization curves of NiFe LDH with various percentages of iR compensation. iR compensation was conducted manually using an EIS method.

100 mA cm^{-2}). However, at large current densities (500 and 1000 mA cm^{-2}), the overpotentials with iR compensation by the EIS method are always larger than those with iR compensation by the CI method. This is because the resistance (R) used for iR compensation varies under different current densities, and is normally larger under a larger current density due to the greater amount

of gas bubbling that results in less efficient mass transport. From this point of view, conducting iR compensation automatically by a CI method is more convincing since this can deliver a variable R value under different current densities.

The percentage of iR compensation also has a significant influence on the overpotential for HER and OER. To provide a possible comparison, we manually determined 80%, 85%, 90%, and 100% iR compensation for HER with $MoNi_4$ and OER with NiFe LDH by an EIS method. As shown in Figs. 3c and 3d, respectively, it is clear that the increasing percentage of iR compensation results in a gradual decrease in the HER and OER overpotentials at different current densities. The percentage of iR compensation has a relatively small role in affecting the overpotential at small current densities below 100 mA cm^{-2}, but when the current density is larger than 100 mA cm^{-2}, the differences between different percentages of iR compensation become larger. To present valid iR compensation and to avoid excessive correction, 85% iR compensation is recommended.

Considering the wide use of alkaline electrolyzers in industry, we further tested the overall water-splitting performance, with and without iR compensation, of the NiFeN||NiMoN electrolyzer, where NiFeN was used as an anode and NiMoN as a cathode. As shown in Fig. 4, the NiFeN||NiMoN electrolyzer exhibits very good activity for overall water splitting with iR compensation. The required voltages are only 1.58, 1.61, 1.75, and 1.83 V at current densities of 50, 100, 500, and 1000 mA cm^{-2}, respectively (Table 3). Without iR compensation, the corresponding voltages increase to 1.62, 1.71, and 2.30 V at current densities of 50, 100, and 500 mA cm^{-2}, respectively. The difference in voltage at the current density of 500 mA cm^{-2} is 0.55 V, which is a considerable value that cannot be eliminated in real electrolyzers. Therefore, for overall water splitting, it must once again be emphasized here that the data without iR compensation are more meaningful. We also measured the performance of a Ni foam and stainless-steel mat (SSM) pair, which is used in industrial alkaline electrolyzers. As shown in Fig. 3, the performance

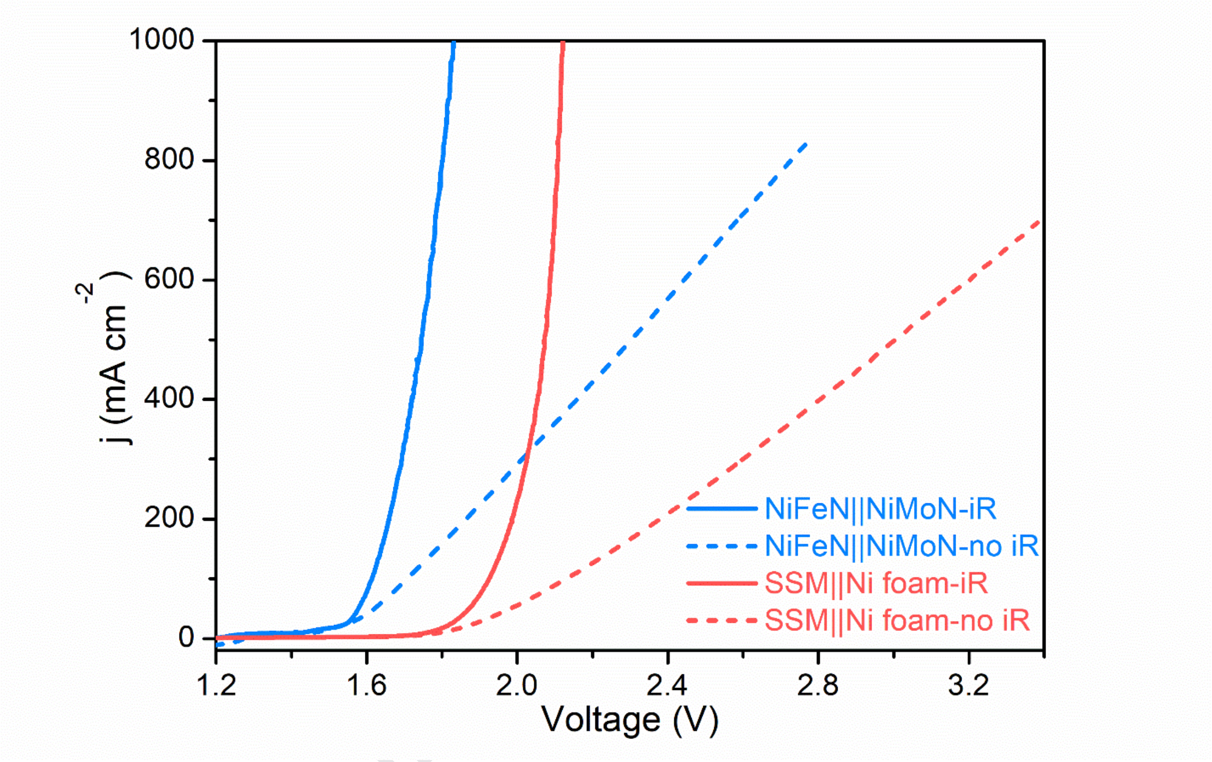

Fig. 4. Polarization curves of different catalysts for overall water splitting in 1 M KOH with and without iR compensation. iR compensation was conducted automatically using a CI method.

of SSM||Ni foam is much worse than that of the NiFeN||NiMoN electrolyzer both with and without iR compensation, indicating that it is still worth developing efficient catalysts based on non-precious materials.

Table 3. Overall water-splitting performance for the two electrolyzers at different current densities with and without iR compensation. Here V_{50}, V_{100}, V_{500}, and V_{1000} represent the voltages at current densities of 50, 100, 500, and 1000 mA cm^{-2}, respectively.

Electrolyzer	iR compensation	V_{50} (V)	V_{100} (V)	V_{500} (V)	V_{1000} (V)
NiFeN‖NiMoN	With	1.58	1.61	1.75	1.83
	Without	1.62	1.71	2.30	N/A
SSM‖Ni foam	With	1.87	1.93	2.07	2.12
	Without	1.98	2.13	3.00	N/A

Catalytic performance without iR compensation is directly related to the R of a catalyst, so reducing R is pivotal for achieving better performance. As mentioned above, for water electrolysis, R mainly includes contact resistance between the catalyst and the substrate, charge-transfer resistance between the catalyst and the electrolyte, and intrinsic resistance of the catalyst. Strategies can be employed to reduce each of these types of resistance. First, using a high-temperature annealing treatment or *in situ* preparation methods to synthesize the catalyst guarantees robust adhesion between the active material and the substrate, thus reducing the contact resistance. Second, constructing unique nanostructures like one-dimensional nanoarrays or two-dimensional ultrathin nanosheets accelerates the charge transfer between the catalyst and the electrolytes, thus decreasing the charge-transfer resistance. Third, element doping or integration with carbon materials enhances the electronic conductivity of the catalyst, thus reducing its intrinsic resistance.

In summary, we have systematically studied and described the influence of iR compensation conducted automatically by a CI method or manually for different percentages by an EIS method on the determination of performance for water electrolysis using the example of several best reported HER and OER catalysts. We found that there is a large difference between overpotential with iR compensation and that without iR compensation, especially when the current density is larger than 50 mA cm^{-2}. The overpotential with iR compensation can be very small, but such small values are always misleading because energy consumption due to R exists in a real electrolysis system. Therefore, the use of overpotential without iR compensation is more practically meaningful for water-electrolysis devices, although this has generally been neglected in the literature thus far. For future reports, we therefore recommend that the overpotential without iR compensation be presented when the current density is larger than 50 mA cm^{-2} in addition to that with iR compensation. This is especially important when the reported catalyst is claimed to be promising for commercial use. Additionally, we found a considerable difference in the voltage required for overall water splitting by an alkaline electrolyzer at large current densities depending on whether iR compensation is applied. Since the considerably higher value without iR compensation cannot be eliminated in real electrolyzers, we likewise recommend that the voltage required by an electrolyzer for overall water splitting be presented without iR compensation when the current density is larger than 50 mA cm^{-2}. With such additional information, those in industry can easily make the decision which catalysts to use for their applications. Finally, to improve catalytic performance without iR compensation, more effort should be devoted to reducing the resistance of catalysts or to exploring efficient alternatives.

Conflict of Interest

The authors declare no competing financial interest.

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- Several HER and OER catalysts were prepared to study the effect of iR compensation.
- There is a very large activity contribution from iR compensation under large current densities.
- The overpotential without iR compensation is more reliable for industrial reference.

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.