Rethinking Electrochemical Deposition of Nickel Oxide for Photovoltaic Applications

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A thin layer of sputtered or wet-processed nickel oxide (NiO_x) is often used to fabricate perovskite solar cells (PSCs). Remarkably, NiO, can also be deposited by a recently developed electrochemical method, which is considered promising due to its short processing time, absence of high-vacuum conditions, and ease of manufacturing. Such electrochemically deposited NiO_x (eleNiO_x) is obtained by applying an electric bias to the front electrode of a PSC or perovskite solar module (PSM). Therefore, the electrode sheet resistance affects the current distribution through it, creating a gradient in the amount of charge provided for the electrochemical reaction. Consequently, this leads to the inhomogeneity in the formed eleNiO_n which has numerous implications on the final photovoltaic performance of PSMs. In this work, the interdependencies between the electrode sheet resistance, current distribution, eleNiOx thickness gradient, and the caused power losses of large area PSMs are discussed. By coupling the experimental findings with our numerical simulations, it is found that heterogeneity in surface potential of even small-sized modules can lead to severe differences in local eleNiO_x thickness and photovoltaic performance. Therefore the potential drop across the front electrode is an inherent problem of this deposition method and potential approaches are proposed to minimize it.

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DOI: 10.1002/solr.202300750

1. Introduction

Hybrid halide perovskite is considered to be the game-changing material for the photovoltaic (PV) industry,^[1] as it offers unique opportunity not only to produce low-cost single-junction PV devices,^[2] but also multi-junction ones.^[3] However, the stability^[4,5] and upscaling^[6,7] of perovskite-based PV remains to be the stumbling blocks of this remarkable technology. While the former could be partially alleviated with a proper encapsulation^[8,9] and backelectrode material,^[10–12] sensitive chargeselective materials, especially hole-selective layers (HSLs), often cause device degradation.^[13] Typically, the HSLs either suffer from decomposition triggered by the hygroscopic salts they contain or from poor homogeneity of the deposition, originating from the complexity to control the process precipitation from the precursor of solution.^[14–16] Thus, nickel oxide (NiO_x) is often considered as a promising HSL due to its robust inorganic structure,^[17] universal

applicability to the most common perovskite compositions and compatibility with industrially relevant processes to coat substrates with superior homogeneity, such as sputtering.^[18] Furthermore, several recent reports have demonstrated high-efficient and stable inverted perovskite solar cells (PSCs) with NiO_x HSL.^[19–21] Consequently, NiO_x can also be effectively used to coat siliconbased substrates for manufacturing multi-junction solar cells.^[22]

While NiO_x sputtering is well-known in the perovskite PV community, other means of depositing it also exist, such as evaporation, deposition from dispersion of pre-synthesized nanoparticles, atomic layer deposition, and electrochemical deposition.^[18] The latter one offers distinct advantages (especially comparing to spin-coating) such as low cost, low material waste, and ability to coat large substrates. Furthermore, unlike sputtering, it does not require vacuum conditions, enabling a simple and fast (<1 min without temperature treatment) deposition process and potentially translating into low fabrication cost.^[23,24] Furthermore, the electrochemical deposition of NiO_x is driven by the electrical contact to which a voltage is applied and thus its homogeneity is primarily determined by the homogeneity of the contact and its properties. Although there have been attempts to demonstrate that the properties of such electrochemically

deposited NiO_x (eleNiO_x) are similar throughout a 1 cm² PSC,^[23] the question whether eleNiO_x will also be homogeneous on a 1 m² PV module is open. Currently, none of the reports discussing electrochemical deposition of metal oxides consider the effect of the electrode sheet resistance (R_{sheet}) on the final performance of a PV device. If perovskite PV is indeed headed for commercialization in the next years, understanding such effects for the large-area coating methods is paramount.

Therefore, in this work, for the first time, we examine this issue and evaluate its impact on the power losses of a photovoltaic device. First, we demonstrate how such $eleNiO_x$ is formed and how to control the deposition process. Next, we use a numerical simulation based on the finite difference method to assess the distribution of the potential at the electrode surface, which drives the $eleNiO_x$ reaction formation. After demonstrating the presence of an $eleNiO_x$ thickness gradient due to heterogeneity in the provided surface charge, we perform optical simulations to link the local $eleNiO_x$ thickness with the photovoltaic performance. Finally, we quantify the local and cumulative power losses due to the spatial heterogeneity in performance and provide methods to minimize them.

2. Results and Discussion

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2.1. Electrochemical Deposition of NiO_x

) Ni²

NO:

NO

A convenient and controllable method to deposit NiO_x electrochemically is to use an aqueous nickel nitrate solution

NO

 $(Ni(NO_3)_2 \cdot 6H_2O)$. In such electrolyte, polar water molecules can dissociate nickel nitrate into Ni^{2+} and NO_3^- ions (**Figure 1**a), where the latter gets further reduced to nitrite according to

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
 (1)

Released hydroxide at the surface reacts with ${\rm Ni}^{2+}$ ions to form the nickel hydroxide polymorph $\alpha\text{-Ni}(OH)_2$ (Figure 1a) according to

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$$
 (2)

After sintering at high temperature, nickel hydroxide decomposes, releasing H_2O gas, which leaves a solid nonstoichiometric NiO_x layer on the substrate which is a p-type semiconductor.

First, we deposited such eleNiO_x on the tin-doped indium oxide (ITO) acting as front-electrode for inverted (p–i–n) PSC. Scanning electron microscope images in Figure S1, Supporting Information, demonstrate that the formed eleNiO_x layer has a high homogeneity and a compact morphology. We note that the grown layer follows the pattern and roughness of the ITO surface (Figure S2, Supporting Information), which is important for effective electron blocking and prevention of shunts in a PSC. Remarkably, eleNiO_x layer as low as \approx 5 nm (Figure 1b) could be deposited suggesting that such process allows to precisely control the layer thickness for an optimal balance between efficient hole transport and low parasitic absorption.

eleNiO

ITO

(b)

H 1 = 5.58 nm

ITO

(Cathode)



Figure 1. a) Illustration of the electrochemical processes taking place during the deposition of Ni(OH)₂ on tin-doped indium oxide (ITO). b) Crosssectional scanning electron microscope images of electrochemically deposited NiO_x (eleNiO_x) on ITO after 5 s of deposition, corresponding to a 5–6 nm thick layer. c) Measured eleNiO_x layer thicknesses after different deposition times. d) Change in absorbance of the ITO + eleNiO_x samples for different eleNiO_x thicknesses.

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To investigate the chemical state and surface nickel compositions of formed eleNiO_x layer, X-ray photoelectron spectroscopy (XPS) measurement was carried out. As shown in Figure S3, Supporting Information, three kinds of nickel $2p_{3/2}$ core-level signals were observed in both films, corresponding to the electronic states of Ni²⁺ (peak at 854.5 eV) in the cubic NiO structure, NiOOH (peak at 856.1 eV), and Ni³⁺ (peak at 857.5 eV). In comparison with the XPS results of films annealed at different temperatures, the NiO peak was significantly enhanced at higher annealing temperature (300 °C) at the surface of eleNiO_x layer, indicating that the higher annealing temperature promotes the decomposition of Ni(OH)₂ to NiO and inhibits the surface hydroxylation. The reduction of hydroxyl contents could result in better interface properties and improve the stability of the perovskite film, which is sensitive to moisture.

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The thickness of the deposited $eleNiO_x$ (*d*) can be approximated via Faraday's law of electrolysis

$$d = I_{\rm dep} M t (z F \rho A)^{-1} \tag{3}$$

where *M* is molar weight, *t* is deposition time, *z* is number of electrons transferred during the electrodeposition, *F* is Faraday constant, ρ is material density, I_{dep} is applied deposition current, and *A* is electrode (cathode) area. In the case of eleNiO_x, the dependency of the layer thickness on the deposition time should follow the linear trend plotted in Figure 1c according to Equation (3). To confirm this relation, we manufactured several eleNiO_x layers by varying the deposition time between 10 and 40 s (Figure S4, Supporting Information), which corresponds to 81.4–325 µC of provided charge. While the mean layer thickness agrees well with theoretically obtained values, thicker layers exhibit significantly higher inhomogeneity resulting in larger spread. The results from the UV–vis measurements in Figure 1d confirm the intuitive assumption that the thicker the eleNiO_x layer is, the higher the light absorption is.

These findings underline two phenomena associated with $eleNiO_x$ layer: 1) its thickness inhomogeneity seems to scale with the amount of provided charge for $eleNiO_x$ growth and 2) thickness plays an important role in photon management, which directly impacts the PSC performance. Single-junction cells with transparent conductive front electrode require a contact point for an application of bias. Concomitantly, the contact point must be above the electrolyte surface level, leading to the downward (i.e., toward the electrolyte) flow of the current (and hence charge) within ITO. Although ITO is a highly conductive material ($R_{sheet} = 10-20 \Omega \text{ sq}^{-1}$), the potential drop between its opposite edges can become significant in a large-area device, especially if its aspect ratio is significantly below 1. Thus, the spatial variation in the bias and charge during the eleNiO_x growth could arise which would result in a thickness gradient of the deposited layer.

2.2. Effect of Electrode Sheet Resistance on the NiO_x Thickness

To estimate the spatial distribution of the electrostatic potential ϕ and deposition current I_{dep} at the surface of the electrode, we first need to consider a 2D mesh consisting of a finite number of nodes (with *x* and *y* as coordinates). Then, the local potential can be described as

$$-\nabla^2 \phi = I_{\rm dep}(\phi_{x,y}) R_0 \tag{4}$$

where $I_{dep}(\phi_{x,y})$ is the local deposition current and R_0 is the nodal resistance. To solve the differential Equation (4), we apply a finite difference method. The discretization of the spatial distribution of ϕ is obtained by approximating the Laplacian operator ∇^2 using neighboring nodal ϕ in a 2D matrix. Concomitantly, the $I_{dep}(\phi_{x,y})$ has to be equal to the sum of the local currents at the neighboring nodes and, therefore, we can rewrite Equation (4) as

$$R_0^{-1}(\phi_{x+1,y} + \phi_{x,y+1} + \phi_{x-1,y} + \phi_{x,y-1} - 4\phi_{x,y}) + I_{dep}(\phi_{x,y}) = 0$$
(5)

Equation (5) is solved for each node $\phi_{x,y}$ iteratively to minimize the deviation until it is converged to an adequate level of accuracy. A similar method has been recently implemented by Guo et al. for a 2D simulation of the solar cell to study the lateral charge transport.^[25] More details on the computation can be found in Note S1, Supporting Information.

A simulated stream plot in **Figure 2**a shows that a potential drop along a cathode (ITO in our case) will produce a gradient in ϕ toward its upper edge, leading to an increase in I_{dep} close to the ITO and concentrating it near its top edge. Intuitively it can be understood by considering that the current follows the path of the least resistance, which in our case lies through the least amount of ITO toward the contact. Hence, less charge flows through the bottom edge of the ITO and less electrons participate in reaction (1), leading to a decreasing rate of OH⁻ and Ni(OH)₂ formation toward the bottom.

To see how critical such inhomogeneity for the operation of a PV device is, we first consider a small mesh of 16×20 tiles with a 1 mm² area each, mimicking a substrate with an ITO area of 3.2 cm^2 . We chose such mesh with a 4:5 aspect ratio, which resembles the typical thin-film module aspect ratio.^[26] Next, we use the same deposition parameters as in our experimental work (Figure 1b–d) to evaluate the I_{dep} distribution in case when a bias is applied via a line contact (as opposed to a point contact, like, e.g., a clamp). Figure 2b demonstrates the presence of a I_{dep} gradient caused by the potential drop in ITO (Figure S5, Supporting Information). However, the difference between the highest and the lowest currents is rather low: <0.01 mA. Note that the I_{dep} map shown in Figure 2b represents the deposition current at each 1 mm² of the ITO and summation over the entire ITO area gives the same current value that was fed in our experiments. Since most of the high-efficient PSCs have a NiO_x thickness of $\approx 20 \text{ nm}$,^[22] we also consider the deposition time corresponding to such $eleNiO_x$ thickness. In this case, the variation in eleNiO_x thickness – d_{eleNiO_x} (Figure 2c) is only marginal (<0.3 nm), which is not expected to contribute significantly to the spatial performance inhomogeneity.

If we consider a larger mesh of 160×200 with an ITO area of 320 cm^2 , resembling a submodule size (according to the definitions accepted by the PV community^[27]), we start to see much more significant potential (Figure S6, Supporting Information), current (Figure 2d), and eleNiO_x thickness (Figure 2e) inhomogeneities. The current at the bottom ITO edge drops by a factor of \approx 31, resulting in eleNiO_x thickness <1 nm. Such tremendous





Figure 2. a) Exemplary "stream plot" showing how a gradient in the applied potential $\nabla \phi$ due to non-negligible cathode sheet resistance can influence the flow of charges in the electrolyte and, thus, current vector field. b) Deposition current distribution on the cathode due to its sheet resistance, resulting in inhomogeneous layer growth and c) varying eleNiO_x thickness. Upscaling the cathode area by a factor of 100 results in a strong increase in inhomogeneity of d) the current distribution and e) eleNiO_x thickness. f) Difference between the eleNiO_x thickness on the bottom and top of the cathode as a function of cathode area.

difference in layer thickness between the opposite edges of the ITO $(d_{eleNiO_x}^{top} - d_{eleNiO_x}^{bottom})$ can have several detrimental effects on the performance of a large PV device. Naturally, larger ITO area leads to larger difference (Figure 2f), which can reach several orders of magnitude, when the ITO area approaches 0.1 m². Note that all the devices considered in Figure 2f have the same aspect ratio of 4:5. We note that this is still significantly below the active area of commercial thin-film modules.^[28] Importantly, here we do not consider additional problems associated with "edge-effects" during the deposition,^[29] which might occur and become problematic for such large substrates. Furthermore, the deposition time in practice might also affect the charge-carrier mobility, defect density, and other fundamental properties important for the solar cell operation. However, these effects are beyond the scope of this work, as we mainly focus here on the optical and photogeneration losses.

2.3. Effect of NiO_x Thickness on the Local Photovoltaic Performance

To evaluate the effect of $eleNiO_x$ inhomogeneity on the power conversion efficiency (PCE), we consider its effects on shortcircuit current density (J_{SC}) and open-circuit voltage (V_{OC}). Both of them can be found from the current density–voltage (J-V) curve of a solar cell, which in the case of the radiative limit can be described according to the well-known ideal diode equation

$$J(V) = J_0 \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) - J_{\rm ph}$$
⁽⁶⁾

where J_0 is dark saturation current density, q is elementary charge, k is Boltzmann constant, T is temperature, and J_{ph} is photocurrent

density. While the photocurrent density arises from the generation of excess carriers ΔG , J_0 is caused by the generation of charge carriers in the dark at T > 0 K– G^0 . Thus, Equation (6) can be rewritten in terms of these generation rates

$$J(V) = qG^{0}(L_{\rm e} + L_{\rm h})\left(\exp\left(\frac{qV}{kT}\right) - 1\right) - q\int_{-L_{\rm h}}^{L_{\rm e}} \Delta G dx \tag{7}$$

where $L_{\rm e}$ and $L_{\rm h}$ are the diffusion lengths of electrons and holes, respectively. Since, both currents result from the generated electron–hole pairs, they can be found from the integrated product of the solar cell's external quantum efficiency (EQE) and the incident energy flux $\Phi_{\rm in}$. Energy flux incident on a solar cell in the dark, causing G^0 , can be approximated by the black-body (BB) radiation at T = 300 K, so that J_0 can be found from

$$J_0 = q \int_{\lambda_{\min}}^{\lambda_{\max}} EQE \,\Phi_{\ln}^{BB} d\lambda = \int_{\lambda_{\min}}^{\lambda_{\max}} EQE \,\frac{2hc^2}{\lambda^5} \frac{1}{\exp(\frac{hc}{\lambda kT}) - 1} \,d\lambda \qquad (8)$$

where *h* is Planck's constant, *c* is speed of light, and λ is photon wavelength. The wavelength interval defined by λ_{\min} and λ_{\max} is chosen by the onset of the EQE and the point where the additional contribution by the BB spectrum can be neglected. Similarly, the J_{ph} caused by ΔG under AM1.5G illumination can be found via

$$J_{\rm ph} = q \int_{-L_{\rm h}}^{L_{\rm e}} \Delta G dx = q \int_{\lambda_{\rm min}}^{\lambda_{\rm max}} {
m EQE} \, \Phi_{\rm in}^{{
m AM1.5G}} d\lambda$$
 (9)

However, here λ_{\min} and λ_{\max} are chosen by the onset of absorption and the point where the glass substrate and ITO become opaque to UV light.

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Thus, if we know the light absorption of each layer of a solar cell, we can obtain its EQE, assuming an ideal (lossless) charge extraction and absence of non-radiative recombination. In this case, $J_{\rm ph}$ and J_0 are limited only by radiative recombination and can be determined via Equation (8) and (9). Here, we use transfer-matrix method (TMM) to calculate the light absorption in each layer of a PSC under AM1.5G illumination, details of which could be found in Note S2, Supporting Information.^[30] Figure 3a shows an absorption profile along the modeled glass/ITO/eleNiO_x/perovskite stack depending on the incident light wavelength. Note that the interference of coherent reflected and transmitted waves at each interface results in the appearance

of "fringes" in the absorption profile. Next, we demonstrate that EQE changes in shape as a function of d_{eleNiO_x} as shown in Figure 3b, which also influences J_{ph} according to Equation (9). Interestingly, the calculated J_{ph} (which we assume is equal to J_{SC}) first increases with higher d_{eleNiO_x} until the latter reaches \approx 40 nm and then decreases (Figure 3c), due to the increase in coherent reflection. Remarkably, we found a similar trend in the rising J_{SC} of our fabricated PSCs (Figure S7, Supporting Information), confirming the validity of our optical simulation. Thus, J_{SC} of PSCs can vary between 21.6 and 22.4 mA cm⁻² depending on the eleNiO_x thickness (Figure 3d).



Figure 3. a) Local wavelength-dependent light absorption along the glass/ITO/NiO_x(20 nm)/perovskite stack obtained from the transfer matrix method. b) Change in the external quantum efficiency (EQE) of a perovskite solar cells (PSC) depending on the eleNiO_x thickness (d_{eleNiO_x}), causing c) change in the photocurrent and short-circuit current density (J_{SC}). d) Change in d_{eleNiO_x} along the PSCs length, affecting the local J_{SC} , open-circuit voltage (V_{OC}), and power conversion efficiency (PCE).



The V_{OC} can be found from the diode equation provided earlier, by considering a situation with no current flow: $J(V_{\text{OC}}) = 0$. That allows to rearrange Equation (6) to give us

$$V_{\rm OC} = \frac{kT}{q} \ln \left(\frac{J_{\rm ph}}{J_0} + 1 \right) \tag{10}$$

which depends primarily on the ratio between the current densities. Since $V_{\rm OC}$ depends logarithmically on $J_{\rm ph}$, it does not change significantly for different $d_{\rm eleNiO_x}$ (Figure 3d). However, we note that if the NiO_x layers are too thin, in practice they might not cover the substrate entirely, resulting in the presence of shunts, potentially bringing down $V_{\rm OC}$ drastically.

Notably, since V_{OC} is significantly below the V_{OC} limit for this energy bandgap, the highest obtainable fill factor (FF) must also be below the FF in the case of Shockley–Queisser limit (FF^{SQ})–90.4%. To estimate the FF of a cell in the absence of any resistive losses (FF₀), we can use the Green equation,^[31] which has been recently proven to be accurate for PSCs^[32,33]

$$FF_0 = \frac{\nu_{oc} - \ln(\nu_{oc} + 0.72)}{\nu_{oc} + 1}$$
(11)

where $v_{oc} = \frac{qV_{OC}}{kT}$. Note that since we consider that the only recombination process is radiative, the reduction in FF₀ relatively to the FF^{SQ} originates from the nonideal photon management, i.e., PSC's EQE, which influences J_0 and V_{OC} .

Finally, with all the information on the local J_{SC} , V_{OC} , and FF, we can calculate the local PCE. We attribute the PCE inhomogeneity of a (hypothetical) 320 cm² PSC (Figure 3d) mainly to the J_{SC} variation, which comes from the d_{eleNiO_x} gradient (Figure 2e).

2.4. Effect of Inhomogeneous Performance on the Minimodule Operation

Although PCE inhomogeneity would result in a certain drop in total power output (Pout), such PSC would still operate close to its maximum potential. However, the situation is slightly different if we consider that such eleNiO_x layer would be used for a 320 cm² minimodule fabrication. Since most single-junction perovskite solar modules (PSM) are manufactured using P1-P2-P3 laser scribing processes, such $eleNiO_x$ layer (together with perovskite and ESLs) would be selectively removed at the interconnects using laser ablation for cell separation. Once the electrode is deposited, all the cells are connected in series. In this case, the layers should be ablated in the longitudinal direction (Figure 4a), rather than transverse (Figure 4b), otherwise the overall module short-circuit current (I_{SC}) would be dictated by the cell producing the lowest $I_{\rm SC}$, with the lowest $d_{\rm eleNiO_v}$. In this case, the excess current generated by cells with thicker eleNiO_x layer would be dissipated in the cell with the thinnest NiO_x (as heat) and not contribute to P_{out} , which could potentially place this cell under reverse bias and lead to rapid perovskite degradation. ¹¹Therefore, in the following, we consider the PV performance inhomogeneity along each cell in 1D, assuming it is the same in each cell of the PSM.

Although Equation (5) is valid for an ideal solar cell with only radiative recombination, for a more realistic scenario of a solar module operation, additional losses due to series and shunt



Figure 4. Two possible ways of cell interconnection in a module: a) longitudinal and b) transverse. The color scale and \times and y dimensions are identical with Figure 2e. c) Current–voltage (*I–V*) curves of a 320 cm² PV minimodule with different number of cells in it. d) Local cell power and corresponding power loss at each 1 mm² along the minimodule length, as well as the cumulative minimodule power loss due to eleNiO_x inhomogeneity.

resistance need to be considered. This can be realized by adding the resistance terms and the associated voltage drop across these resistors to Equation (6), which are placed according to the onediode solar cell equivalent circuit. Neglecting the "-1" in Equation (5) (since the exponential term » 1), the *J*–*V* curve can be described by

$$J(V) = J_0 \exp\left(\frac{q(V+JR_s)}{kT}\right) + \frac{(V+JR_s)}{R_p} - J_{ph}$$
(12)

where R_s is the series resistance and R_p is the parallel, i.e., shunt resistance. Assuming R_s of $1.2 \Omega \text{ cm}^2$ and R_p of $10 \text{ k}\Omega \text{ cm}^2$, the PSC with a 40 nm eleNiO_x layer would have 21.4% PCE with a current–voltage (*I*–*V*) curve as shown in Figure 4c. Simulation of the local *I*–*V* curves (according to Equation (12)) was done by applying an open-source code developed by Holmgren et al.^[34]



to our generated 2D mesh (more details can be found in Note S3, Supporting Information).

An increase in number of cells in a PSM reduces the individual cell area and therefore decreases the $I_{\rm ph}$ of each cell. Since the cells are interconnected in series, the current (including the $I_{\rm SC}$) running through them is the same and the PSM's total voltage is the sum of voltage drops across each cell (Figure 4c). Hence, the total $P_{\rm out}$ and PCE are not changed significantly between the I-Vcurves, with only a small reduction in $I_{\rm ph}$ due to the "dead area" of the interconnects.

Figure 4d demonstrates that the local P_{out} becomes reduced in the presence of the resistive losses and decreases with thinner eleNiO_x layers. Considering the difference between the most efficient region of a cell and each local P_{out} , we quantify the total power loss, relative to its "potential P_{out} " (Figure 4d). Furthermore, integrating the local power loss over the entire minimodule length and multiplying it by the width allows us to quantify the cumulative power loss of a minimodule. This result demonstrates that even small variations in d_{eleNiO_x} can cause reduction in P_{out} when we consider large PV devices. And, the variation in d_{eleNiO_x} is a direct effect of the variation in I_{dep} , which is caused by the sheet resistance of the ITO during the electrochemical deposition process.

2.5. Perspective

With this in mind, one realizes that the issues described in this work are inevitable in the electrochemical deposition process for PV applications. Especially in the case of electrochemically deposited perovskite layers which have recently gained some attention in the community,^[35–38] this becomes a critical problem, since the small variations in thickness will influence the $J_{\rm ph}$ and current mismatch between cells even more than the eleNiO_x inhomogeneity. We postulate that a large PV device with any electrochemically deposited layers has a certain power loss originating from the resistivity of the electrode. The only two solutions to this problem could potentially be 1) highly conductive front electrode and 2) application of bias through the substrate to eliminate spatial $I_{\rm dep}$ inhomogeneity.

Method (1) is limited, since the front electrode of a PSM should be highly transparent for reaching high $J_{\rm ph}$ and PCE, and most of the highly conductive materials are opaque metals. However, fluorine-doped tin oxide (FTO) could potentially reduce the inhomogeneity, due to its lower sheet resistance than ITO (typically 7 Ω sq⁻¹ for FTO and 15 Ω sq⁻¹ for ITO). Figure S8, Supporting Information, demonstrates how an improvement in conductivity of the front electrode by 1 order of magnitude strongly reduces the inhomogeneity of the deposited eleNiO_x, photocurrent, and consequently performance losses.

Method (2) is even more challenging, since most of the transparent substrates are insulators (e.g., glass, polymers). Up to date, there are no transparent conductive or semiconductive substrates demonstrated that could be considered for PV applications.

Therefore, further research of the electrochemical deposition of semiconducting layers for PV application should focus on finding transparent and highly conductive front electrodes and/or substrates for PV devices.

3. Conclusions

In the presented study, we have demonstrated the electrochemical deposition of the hole-selective NiO_x layer (eleNiO_x) for PV devices can be deposited electrochemically with high control over the layer thickness. But more importantly, for the first time, we highlight an inherent problem of this deposition method: the non-negligible sheet resistance of the deposition electrode, which is the front electrode of a PV device. By combining the finite difference simulation of current distribution through the front electrode, we show that the sheet resistance can cause a strong gradient in the deposition current along the electrode. More specifically, the deposition current, participating in the electrochemical reaction can vary by more than one order of magnitude between the opposite edges of the deposition electrode, consequently, leading to a dramatic variation in eleNiO_x thickness (40 nm on one electrode edge and <1 nm on the opposite edge). Due to nonlinear effect on eleNiO_x thickness, our TMM simulation quantifies the effect of optical loss on the *I*-V parameters of the solar cells and modules, showing that the local PCE can vary by as much as $1\%_{abs}$ due to the eleNiO_x thickness gradient. Finally, we also show that PV minimodules with such inhomogeneous layers would lose more than 10 W only due to this issue. The presented findings demonstrate an "optimistic scenario", with no additional non-radiative recombination losses and low shunt resistance problems caused by the low eleNiO_x thickness, which are likely to occur in practice. Furthermore, we also present guidelines to minimize these issues by selecting electrodes with lower sheet resistance or by implementing a conductive substrate, where the bias can be applied through the opposite face. We encourage researchers investigating this deposition method to find effective approaches to solve this challenging problem to be used in the PV applications and bring emerging technologies such as perovskite PV closer to their commercialization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was conducted within an internal project funded by Fraunhofer ISE. In addition, this work was partially funded by the Horizon Europe framework program for research and innovation under grant agreement no. 101084124 (DIAMOND) and through Swiss National Science Foundation with project no. 200020_185041. The authors thank Xiaobo Zhou for valuable suggestions.

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

D.B. conceived the idea, organized the experimental and analytical work, analyzed all data, wrote the manuscript, and prepared the figures; U.K.D. has cleaned the substrates and measured the transmittance and



reflectance of the fabricated samples; S.K. and J.E. have developed the layer deposition process, whereas J.E. and D.B. fabricated all the samples; J.S. and B.Y. conducted XPS measurements; H.M. measured the layer thickness and G.L. analyzed the data; C.B. wrote the script for finite difference method calculation of the spatial potential and current distribution; C.B. also integrated the transfer-matrix method into a new script for iteratively calculating wavelength-dependent absorption, calculated the (theoretical) device EQE, and integrated its product with the AM1.5G spectrum over the relevant wavelength range. In addition, C.B. and D.B. wrote a script to calculate the dark photon flux originating from the product of EQE and BB spectrum at T = 300 K to calculate the local dark saturation current J_0 ; D.B. calculated the V_{OC} and FF^0 based on the simulated spatially dependent J_{ph} and J_0 , implemented the python script to account for the resistance effects, and calculated the module power, as well as the power losses originating from the eleNiO_x thickness inhomogeneity; M.K. and U.W. provided valuable suggestions to the manuscript and participated in editing the manuscript. All authors read and commented on the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrochemistry, nickel oxide, perovskites, photovoltaics, solar cells, solar modules

Received: September 20, 2023 Revised: November 8, 2023 Published online:

- J.-P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt, *Science* 2017, 358, 739.
- [2] Z. Li, T. R. Klein, D. H. Kim, M. Yang, J. J. Berry, M. F. A. M. van Hest, K. Zhu, Nat. Rev. Mater. 2018, 3, 18017.
- [3] F. Fu, J. Li, T. C.-J. Yang, H. Liang, A. Faes, Q. Jeangros, C. Ballif, Y. Hou, Adv. Mater. 2022, 34, 2106540.
- [4] Q. Wang, N. Phung, D. Di Girolamo, P. Vivo, A. Abate, *Energy Environ. Sci.* 2019, 12, 865.
- [5] P. Holzhey, M. Saliba, J. Mater. Chem. A 2018, 6, 21794.
- [6] Y. Rong, Y. Hu, A. Mei, H. Tan, M. I. Saidaminov, S. I. Seok, M. D. McGehee, E. H. Sargent, H. Han, *Science* 2018, 361, aat8235.
 [7] N. C. Bark, K. Zhu, Nat. Pay. Mater. 2020, 5, 323.
- [7] N.-G. Park, K. Zhu, Nat. Rev. Mater. 2020, 5, 333.
- [8] R. Cheacharoen, C. C. Boyd, G. F. Burkhard, T. Leijtens, J. A. Raiford, K. A. Bush, S. F. Bent, M. D. McGehee, *Sustainable Energy Fuels* 2018, 2, 2398.
- [9] Damp Heat, Temperature Cycling and UV Stress Testing of Encapsulated Perovskite Photovoltaic Cells: (A Joint Conf. 45th IEEE PVSC, 28th PVSEC & 34th EU PVSEC), (Ed: IEEE), IEEE, Piscataway, NJ, June 2018.
- [10] D. Bogachuk, S. Zouhair, K. Wojciechowski, B. Yang, V. Babu, L. Wagner, B. Xu, J. Lim, S. Mastroianni, H. Pettersson, A. Hagfeldt, A. Hinsch, *Energy Environ. Sci.* **2020**, *13*, 3880.
- [11] D. Bogachuk, K. Saddedine, D. Martineau, S. Narbey, A. Verma, P. Gebhardt, J. P. Herterich, N. Glissmann, S. Zouhair, J. Markert, I. E. Gould, M. D. McGehee, U. Würfel, A. Hinsch, L. Wagner, *Sol. RRL* 2022, *6*, 2100527.

- [12] A. Mei, Y. Sheng, Y. Ming, Y. Hu, Y. Rong, W. Zhang, S. Luo, G. Na, C. Tian, X. Hou, Y. Xiong, Z. Zhang, S. Liu, S. Uchida, T.-W. Kim, Y. Yuan, L. Zhang, Y. Zhou, H. Han, *Joule* **2020**, *4*, 2646.
- [13] G.-W. Kim, G. Kang, M. Malekshahi Byranvand, G.-Y. Lee, T. Park, ACS Appl. Mater. Interfaces 2017, 9, 27720.
- [14] K. Liu, Y. Yao, J. Wang, L. Zhu, M. Sun, B. Ren, L. Xie, Y. Luo, Q. Meng, X. Zhan, *Mater. Chem. Front.* 2017, 1, 100.
- [15] Z. Hawash, L. K. Ono, S. R. Raga, M. V. Lee, Y. Qi, Chem. Mater. 2015, 27, 562.
- [16] T. Zhang, F. Wang, H.-B. Kim, I.-W. Choi, C. Wang, E. Cho, R. Konefal, Y. Puttisong, K. Terado, L. Kobera, M. Chen, M. Yang, S. Bai, B. Yang, J. Suo, S.-C. Yang, X. Liu, F. Fu, H. Yoshida, W. M. Chen, J. Brus, V. Coropceanu, A. Hagfeldt, J.-L. Brédas, M. Fahlman, D. S. Kim, Z. Hu, F. Gao, *Science* **2022**, *377*, 495.
- [17] J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. M. Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. de Marco, Y. Yang, *Nat. Nanotechnol.* **2016**, *11*, 75.
- [18] X. Yin, Y. Guo, H. Xie, W. Que, L. B. Kong, Sol. RRL 2019, 3, 1900001.
- [19] C. Zhang, H. Li, C. Gong, Q. Zhuang, J. Chen, Z. Zang, *Energy Environ. Sci.* 2023, 16, 3825.
- [20] Q. Zhuang, H. Li, C. Zhang, C. Gong, H. Yang, J. Chen, Z. Zang, Adv. Mater. 2023, 35, 2303275.
- [21] H. Li, C. Zhang, C. Gong, D. Zhang, H. Zhang, Q. Zhuang, X. Yu, S. Gong, X. Chen, J. Yang, X. Li, R. Li, J. Li, J. Zhou, H. Yang, Q. Lin, J. Chu, M. Grätzel, J. Chen, Z. Zang, *Nat. Energy* **2023**, *8*, 946.
- [22] S. Zhumagali, F. H. Isikgor, P. Maity, J. Yin, E. Ugur, M. de Bastiani, A. S. Subbiah, A. J. Mirabelli, R. Azmi, G. T. Harrison, J. Troughton, E. Aydin, J. Liu, T. Allen, A. U. Rehman, D. Baran, O. F. Mohammed, S. de Wolf, *Adv. Energy Mater.* **2021**, *11*, 2101662.
- [23] I. J. Park, G. Kang, M. A. Park, J. S. Kim, S. W. Seo, D. H. Kim, K. Zhu, T. Park, J. Y. Kim, *ChemSusChem* **2017**, *10*, 2660.
- [24] A. S. Subbiah, A. Halder, S. Ghosh, N. Mahuli, G. Hodes, S. K. Sarkar, J. Phys. Chem. Lett. 2014, 5, 1748.
- [25] H. Guo, Q. Sun, Q. Zhang, H. Zhang, L. Yao, C. Xue, Y. Wu, Y. Tang, R. Liu, AIP Adv. 2022, 12, 015322.
- [26] E. J. Wolf, I. E. Gould, L. B. Bliss, J. J. Berry, M. D. McGehee, Sol. RRL 2022, 6, 2100239.
- [27] M. A. Green, E. D. Dunlop, G. Siefer, M. Yoshita, N. Kopidakis, K. Bothe, X. Hao, Prog. Photovoltaics 2023, 31, 3.
- [28] First Solar, https://www.firstsolar.com/-/media/First-Solar/Technical-Documents/User-Guides/Series-6-User-Guide.ashx?la=en (accessed: April 2023).
- [29] G. Yang, D. Deng, Y. Zhang, Q. Zhu, J. Cai, *Electrocatalysis* 2021, 12, 478.
- [30] National Renewable Energy Laboratory (NREL), https://www.nrel. gov/grid/solar-resource/spectra-am1.5.html (accessed: March 2023).
- [31] M. A. Green, Sol. Cells 1982, 7, 337.
- [32] B. Yang, J. Suo, F. Di Giacomo, S. Olthof, D. Bogachuk, Y. Kim, X. Sun, L. Wagner, F. Fu, S. M. Zakeeruddin, A. Hinsch, M. Grätzel, A. Di Carlo, A. Hagfeldt, ACS Energy Lett. 2021, 6, 3916.
- [33] S. Zouhair, B. Luo, D. Bogachuk, D. Martineau, L. Wagner, A. Chahboun, S. W. Glunz, A. Hinsch, Sol. RRL 2022, 6, 2100745.
- [34] W. F. Holmgren, C. W. Hansen, M. A. Mikofski, J. Open Source Software 2018, 3, 884.
- [35] M. Al Katrib, L. Perrin, E. Planes, Sol. RRL 2022, 6, 2200777.
- [36] H. Chen, Z. Wei, X. Zheng, S. Yang, Nano Energy 2015, 15, 216.
- [37] D. Liu, K. Liu, Y. Liu, J. Bai, M. Dai, F. Liu, G. Lu, Sol. Energy 2020, 212, 275.
- [38] J. Yadav, Q. Liang, S. Pan, J. Phys. Chem. C 2020, 124, 10659.