

The Origin of Photoinduced Capacitance in Perovskite Solar Cells: Beyond Ionic-to-Electronic Current Amplification

Wookjin Choi, Sung Won Song, Se Gyo Han, and Kilwon Cho*

Photoinduced capacitances of perovskite solar cells exhibit peculiarities such as an apparently high capacitance and an inductive feature, so-called negative capacitance, which are not easily explained with typical carrier dynamics. Consequently, the origins of the photoinduced capacitances in perovskite solar cells have been intensively debated over the past several years. Here, the photoinduced capacitances of perovskite solar cells are analyzed by impedance spectroscopy. The analysis clarifies that the photoinduced capacitances of perovskite solar cells comprise several Debye relaxation-type capacitance components. Among these components, the photoinduced capacitance in the low-frequency range is attributed to ionic-to-electronic current amplification. However, the photoinduced capacitances in the middle- and high-frequency ranges originate from bipolar injection. The clear elucidation of the origins of the photoinduced capacitances in perovskite solar cells provides comprehensive insights for analyzing properties of perovskites in either the time or frequency domain.

1. Introduction

Impedance spectroscopy is a powerful method to investigate the electronic properties of materials by scrutinizing their electrical responses on various time scales. Sinusoidal current responses with different frequencies provide clues to charge carrier dynamics in materials via an estimated equivalent circuit. Therefore, impedance spectroscopy has been used to evaluate charge carrier mobility,^[1] structural disorder,^[2] and the energetic distribution of carrier traps^[3,4] in various materials. In the same context, impedance spectroscopy has been applied to investigate halide perovskites (PVSKs), which have rapidly become one of the most attractive materials in the photovoltaic community, with the primary objective of analyzing the trap distribution in PVSK solar cells.^[5–12] However, careful consideration is necessary to analyze the impedance of PVSK solar cells because PVSKs exhibit high ionic conductivity, which affects their electrical responses during impedance spectroscopy measurements.

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Recently, a very large capacitance was reported to be induced by light illumination of PVSK solar cells.^[13] Bisquert and co-workers showed that the capacitance measured under 1 sun illumination was three to four orders of magnitude greater than that measured under dark conditions. This huge photoinduced capacitance has not been observed in materials other than PVSK.^[14] This surprising aspect of PVSK solar cells has been attributed to ferroelectric effects, a photoinduced giant dielectric constant,^[13] the accumulation of ionic charges,^[15] and surface charge accumulation.^[16,17] However, these explanations do not fully account for this phenomenon because such very large capacitances ($>10^{-3}$ F cm⁻²) can only occur with an unphysically small separation length (<1 Å) between compensating charges.^[18] Furthermore, PVSK solar cells

sometimes show an inductive loop, so-called negative capacitance, under light illumination.

For an electronic device at near equilibrium, a negative capacitance or resistance is not reasonable because such elements would violate the principles of thermodynamics. Nevertheless, far from equilibrium, e.g., under a high direct-current (DC) bias, a negative capacitance is not prohibited by thermodynamics. A negative capacitance has been observed in various electronic devices, including Schottky diodes,^[19] short based p–n junctions,^[20,21] organic light-emitting diodes,^[22–26] and various types of solar cells.^[27,28] Inductive features are also found in electrochemical measurements involving electrocatalysis, electrodeposition, and electrodissolution.^[29–31] However, the origin of photoinduced negative capacitance in PVSK solar cells remains a debated topic^[32–34] because it should be explained with the involvement of the light illumination.

Very recently, the large capacitance of PVSK solar cells under illumination has been proposed to originate from phase-delayed transient current through devices, not a charge accumulation-and-release process.^[35–37] Because it is relevant to resistive components rather than capacitive ones, the magnitude of the photoinduced capacitance is not limited. Pockett et al. noted that a frequency-dependent recombination process is potentially the origin of photoinduced capacitance in PVSK solar cells.^[35] Thereafter, Moia et al. established an ionic-to-electronic current amplification model that clearly reproduces the photoinduced impedance change.^[36] Furthermore, Ebadi et al. showed that the transient current dynamics is closely related to photoinduced capacitance, strongly supporting the

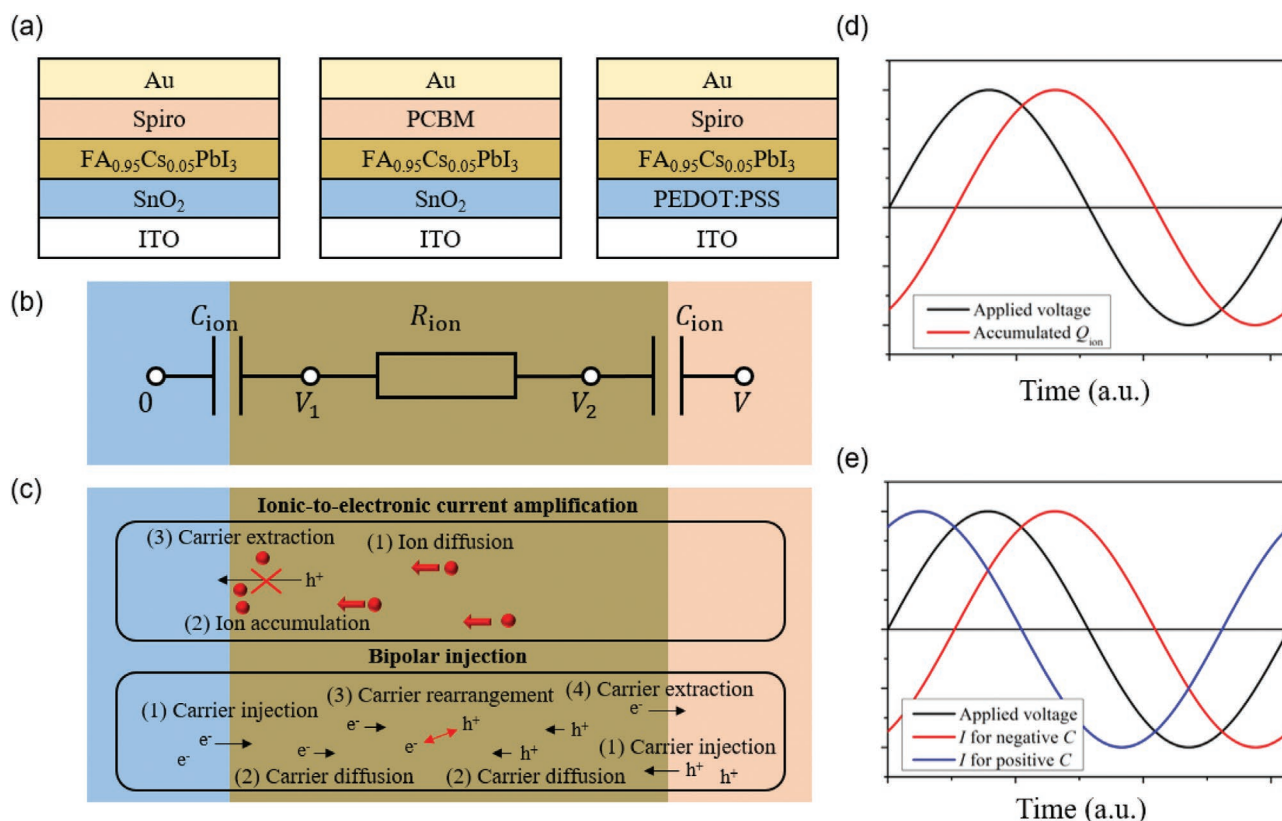


Figure 1. a) Device structures of normal perovskite device, *e*-only device, and *h*-only device. b) Equivalent circuit of device for ionic species. R_{ion} and C_{ion} denote the ionic resistance and the ionic capacitance, corresponding to ionic double layer capacitance formed at interface, respectively. c) The conceptual illustration for two mechanisms of photoinduced capacitance; ionic-to-electronic current amplification and bipolar injection. Ionic-to-electronic current amplification is dominant in low frequency range while bipolar injection is prevailing in high frequency range. d) The accumulation of ionic species at interfaces is always delayed compared to the phase of the applied voltage. e) The phase-delayed current corresponds to the “negative” capacitance whereas the “positive” capacitance means that the phase of the electrical current precedes that of the applied voltage.

ionic-to-electronic current amplification model.^[37] However, the origins and mechanism of switching between negative and positive capacitance still remain unclear despite the establishment of a basic theoretical model. Here, we show that several components correspond to the different frequency dependence of photoinduced capacitances in PVSK solar cells. Furthermore, it is clarified that the origin of the photoinduced capacitance in the low-frequency range differs from that in the high-frequency range. These results indicate that careful consideration is necessary to analyze photoinduced capacitance on the basis of the ionic-to-electronic current amplification model.

2. Results and Discussion

2.1. Ionic-to-Electronic Current Amplification

For the impedance spectroscopy measurements, a total voltage difference, V , was applied across the PVSK solar cell devices; this potential difference comprises a DC voltage, $\bar{V}$, including the quasi-Fermi level difference between holes and electrons under illumination, and an alternating-current (AC) voltage, v , corresponding to a small periodic voltage perturbation: $V = \bar{V} + v = \bar{V} + \tilde{V}e^{i\omega t}$, where $\tilde{V}$ and ω denote the amplitude and

the angular frequency of the AC voltage, respectively. To demonstrate the ionic-to-electronic current amplification model, a planar heterojunction-type structure is fabricated for the PVSK solar cells (Figure 1a). For ionic species in PVSK, the device is equivalent to a resistor–capacitor structure comprising a bulk ionic resistance, R_{ion} , and two ionic double-layer capacitances, C_{ion} , at interfaces between the PVSK and other layers (e.g., an electron transfer layer, hole transfer layer, or electrode) (Figure 1b). Applied voltages induce drift motion of ionic species, leading to accumulation of ionic charges at interfaces. These ionic charges can modulate the carrier extraction rate, resulting in an increase or decrease of the total electrical current (Figure 1c). However, ionic motion is much slower than electrical response, resulting in phase change of the electrical current. Although this current is indeed the DC current through the device, it is measured as a capacitive or inductive element because of the phase delay. This phase-delayed current modulation is a predominant component in AC current, leading to the giant capacitance of PVSK solar cells.

It should be noted that the accumulation of the ionic species is always delayed compared to the phase of the applied voltage (Figure 1d). If ion accumulation increases the total electrical current, it would make the phase-delayed current corresponding to the “negative” capacitance. By contrast, the

“positive” capacitance means the phase of the electrical current precedes that of the applied voltage. It can be generated only when the accumulated ionic species reduce the total electrical current (Figure 1e). In the ionic-to-electronic current amplification model, it is generally believed that accumulated ionic species amplify the injection current by modulating the injection barrier. However, for general solar cell devices, the contacts of active layer are typically Ohmic, corresponding to no injection barrier, so that injection current cannot be further improved by ion movement. Furthermore, current amplification by ion accumulation cannot generate the positive capacitance while photo-induced capacitance of PVSK solar cells is usually positive. Therefore, the carrier extraction process should be mainly discussed in the ionic-to-electronic current amplification model. The photoinduced capacitance is measured under illumination. In this situation, the main component of the total current is photogenerated carriers rather than injected carriers from electrodes. The electric field is screened by ion accumulation, resulting in the reduced extraction of photogenerated carriers, corresponding to the “positive” capacitance.

The amount of charge accumulated at interface is determined by the electrical potential of ionic species at the interface. As expected from the equivalent circuit of the ionic branch (Figure 1b), the electric potential for ionic species at both interfaces is expressed as

$$\begin{aligned} V_1 &= \frac{\bar{V}}{2} + \frac{v}{2} \left(\frac{1}{1 + i\omega R_{\text{ion}} C_{\text{ion}} / 2} \right) \\ V_2 = V - V_1 &= \frac{\bar{V}}{2} + \frac{v}{2} \left(2 - \frac{1}{1 + i\omega R_{\text{ion}} C_{\text{ion}} / 2} \right) \end{aligned} \quad (1)$$

Therefore, the oscillating component of accumulated ionic charges is given by

$$\tilde{Q}_{\text{ion}} = C_{\text{ion}} \tilde{V}_1 = \frac{C_{\text{ion}} v}{2} \left(\frac{1}{1 + i\omega R_{\text{ion}} C_{\text{ion}} / 2} \right) \quad (2)$$

The change of the total current density, J , would be proportional to the accumulated ionic charges because ionic charges at the interface modulate the charge extraction rate. This modulation would be a predominant component in AC current, $\tilde{J}$, because the electrical current through the PVSK solar cell is very large under illumination. Therefore, AC current is expressed as

$$\begin{aligned} \tilde{J} = \tilde{Q}_{\text{ion}} \frac{dJ}{dQ_{\text{ion}}} &= \frac{v}{2Z_{\text{ion}}} \left(\frac{1}{1 + i\omega R_{\text{ion}} C_{\text{ion}} / 2} \right) \\ Z_{\text{ion}} &= \left(C_{\text{ion}} \frac{dJ}{dQ_{\text{ion}}} \right)^{-1} \end{aligned} \quad (3)$$

The apparent capacitance, C_{app} , measured in impedance spectroscopy is derived from the imaginary part of the AC current

$$C_{\text{app}} = -\frac{\text{Im}(\tilde{J})}{\omega v} = \frac{R_{\text{ion}} C_{\text{ion}}}{4Z_{\text{ion}} (\bar{V})} \left(\frac{1}{1 + \left(\frac{\omega R_{\text{ion}} C_{\text{ion}}}{2} \right)^2} \right) \quad (4)$$

Equation (4) provides the frequency as well as the ionic resistance dependence of the measured apparent capacitance. This equation shares the same expression as Debye relaxation

$$C_{\text{app}} = \left(\frac{C_0}{1 + (\omega\tau)^2} \right) \quad (5)$$

where $C_0 = R_{\text{ion}} C_{\text{ion}} / 4Z_{\text{ion}}$ and $\tau = R_{\text{ion}} C_{\text{ion}} / 2$. It should be noted that the DC bias induced by quasi-Fermi level under illumination induces large short circuit current, which allows the large apparent capacitance for PVSK solar cells. However, because the capacitance is AC component, it is not directly involved in the calculation of apparent capacitance.

Apparent capacitance is expected to increase with increasing the film thickness in the case of sufficiently thin PVSK because the ionic resistance, which generates the phase delay, is proportional to the film thickness. Thicker PVSK solar cells have been demonstrated to exhibit larger photoinduced capacitance.^[16,17] However, Equation (4) explicitly predicts a decrease of the apparent capacitance if the film is thicker than the critical thickness where $\omega R_{\text{ion}} C_{\text{ion}} / 2$ equals to unity. We first investigated the film thickness dependence of the apparent capacitance to demonstrate the ionic-to-electronic current amplification model. The apparent capacitances measured at 1 Hz are well matched to the simulation model based on Equation (4) (Figure 2a). This correlation is strong evidence in support of an ionic-to-electronic current amplification model because the surface-charge accumulation model predicts a constant photoinduced capacitance that is independent of the film thickness. The red line represents the capacitance simulated on the basis of parameters $C_{\text{ion}} = 100$ nF and $Z_{\text{ion}} = 500$ Ω , corresponding to a specific capacitance of 1 $\mu\text{F cm}^{-2}$, and $\rho_{\text{ion}} = 4 \times 10^{10}$ $\Omega \text{ cm}$, which provides the closest correspondence to the experimental results. These parameters are consistent with the values of 10^{-5} – 10^{-7} F cm^{-2} and 10^9 – 10^{10} $\Omega \text{ cm}^{-2}$ used by Moia et al. in their circuit simulation.^[36] However, the experimental data and the simulated capacitance differ slightly for devices thicker than 500 nm (Figure 2a). This difference might originate from the fact that apparent capacitance is not determined by only a single component. This aspect will be discussed in detail in the next section.

2.2. Plural Components in Photoinduced Capacitances

We next investigated the illumination power dependence of the photoinduced capacitance (Figure 2b). Here, “photoinduced capacitance” refers to the difference between the capacitance measured under illumination, $C(I)$, and that measured under dark conditions, C_{dark} , corresponding to $\Delta C = C(I) - C_{\text{dark}}$. Thus, the effect of only ionic-to-electronic current amplification can be investigated through analysis of the photoinduced capacitance because the chemical capacitance induced by carrier trapping is included in the capacitance in the dark condition. The measured photoinduced capacitance at low frequencies increases with increasing illumination power, consistent with previous reports,^[16,17,38,39] this behavior originates from the increase of C_0 , corresponding to the decrease of Z_{ion} (Table S1, Supporting Information). For solar cells in

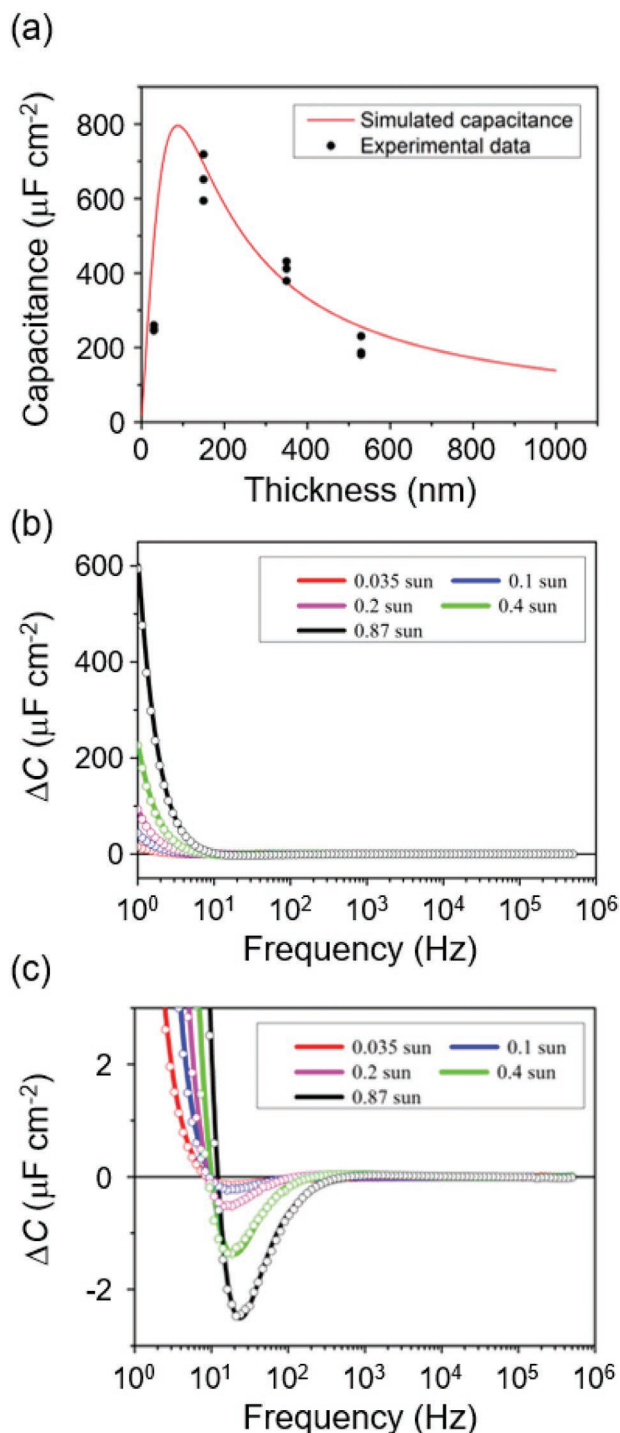


Figure 2. a) Film thickness dependence of apparent capacitance measured at 1 Hz. Simulated capacitance is calculated based on the ionic-to-electronic current amplification model with the circuit parameters of $Z_{\text{ion}} = 500 \, \Omega$, $C_{\text{ion}} = 100 \, \text{nF}$ corresponding to $1 \, \mu\text{F cm}^{-2}$ of specific capacitance, and $\rho_{\text{ion}} = 4 \times 10^{10} \, \Omega \, \text{cm}$. b) The frequency dependence of the photoinduced capacitance under various illumination power. The photoinduced capacitance means the difference between the capacitance under illumination and in dark condition. c) The enlarged version of (b). Negative capacitance is observed in middle frequency range.

recombination regime, the current through PVSK solar cells follows the Shockley equation

$$J = J_s \left(e^{\frac{eV}{nkT}} - 1 \right) + J_{\text{ph}} \quad (6)$$

where J_s , J_{ph} , n , T , e , and k denote the saturation current, the photocurrent, diode ideality factor, the temperature, the elementary charge, and the Boltzmann constant, respectively. Therefore, when the quasi-Fermi level difference across the PVSK device increases in response to the increase of the illumination power, the variation of the current modulated by potential difference is increased, leading to a decrease of Z_{ion} . However, the diffusivity of ionic species barely depends on the applied electric field, resulting in a nearly constant ionic resistance for all of the illumination power.

By contrast, a negative capacitance is observed in the middle-frequency range (10^1 – 10^2 Hz) whereas a positive capacitance is prominent in the low-frequency range ($<10^1$ Hz) (Figure 2c). Furthermore, a small positive or negative capacitance is observed in the high-frequency range ($>10^2$ Hz) (Table S1, Supporting Information). This frequency dependence cannot be reproduced by Equation (4) because this equation cannot express both positive and negative capacitance. Thus, the photoinduced capacitance of PVSK originates from plural sources

$$\Delta C = \sum_{i=1}^n \frac{C_i}{1 + (\omega\tau_i)^2} \quad (7)$$

At least three components are necessary to clearly fit the frequency dependence of photoinduced capacitance, which might explain the small disagreement between the measured photoinduced capacitances and the simulation model based on Equation (4). PVSK solar cells contain various ionic species, including Pb^{2+} , FA^+ , and I^- (the main components of PVSK) as well as Cs^+ (the additive in PVSK) or Li^+ and Co^{3+} (the additives in the interlayer). Therefore, devices with no additives were fabricated to clarify the origin of the ionic-to-electronic current amplification process.

2.3. Photoinduced Capacitances by Bipolar Injection

The photoinduced capacitances of additive-free devices were investigated to confirm the origin of photoinduced capacitance for each frequency range. Among the additives, Cs^+ showed no effect on photoinduced capacitances; it can therefore be excluded as the origin of ionic-to-electronic current amplification (Figure 3a,b). By contrast, the removal of additives associated with the interlayer substantially modified the photoinduced capacitances (Figure 3c,d). Additives are known to dope carriers into the interlayer, leading to an increase of the conductivity and to the suppression of the recombination at interfaces.^[40,41] However, such effects would be excluded from the calculation of photoinduced capacitances because the carrier doping from additives is independent of light illumination. Nevertheless, the frequency range for negative capacitances was substantially changed by elimination of the additives in the

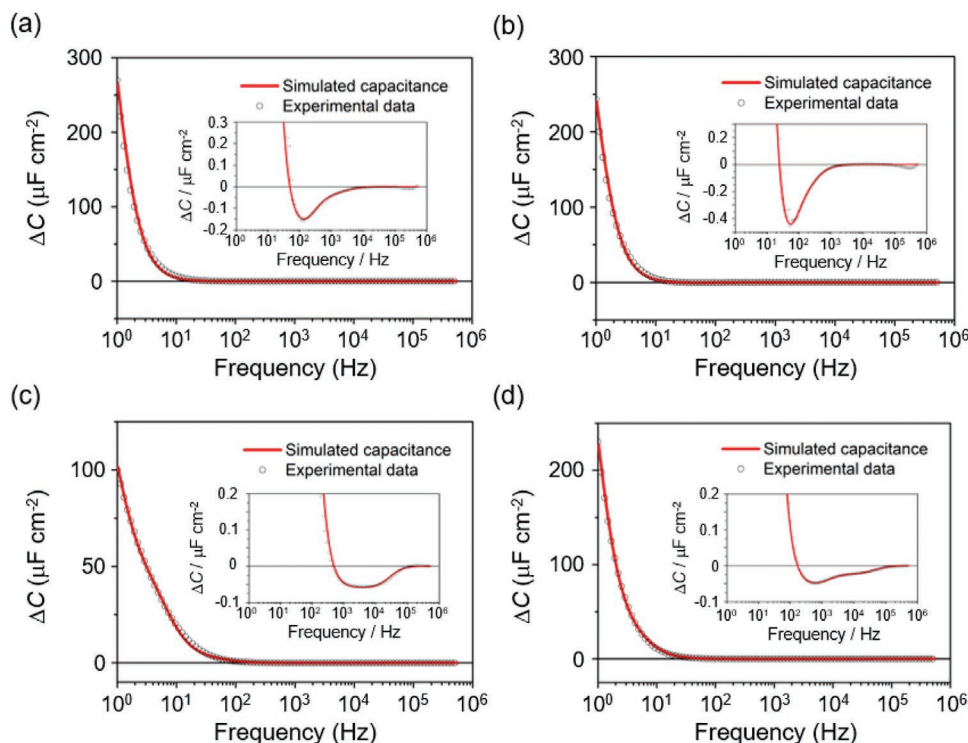


Figure 3. The photoinduced capacitance spectra measured under 0.4 sun for a) the normal perovskite device, b) the device without Cs^+ , c) the device without Li^+ , and d) the device without both Cs^+ and Li^+ .

interlayer. Furthermore, at least four components are necessary to fit the frequency dependence of photoinduced capacitances for the additive-free device (Table S2, Supporting Information), which is obviously too many components because only three ionic species, i.e., Pb^{2+} , FA^+ , and I^- , are present in the device. This result implies that another mechanism, which is relevant to Debye relaxation, is involved in the photoinduced capacitance in addition to the ionic-to-electronic current amplification.

Bipolar injection has been reported to induce a negative capacitance in diode-type devices. The theoretical basis of the negative capacitance induced by bipolar injection has been intensively investigated by Laux et al.^[21] and Gommans et al.^[42,43] The charge carrier dynamics are described by the drift-diffusion equations

$$\begin{aligned} \nabla \cdot (\epsilon \nabla \phi) &= e(n - p) \\ \nabla \cdot J_n &= e \left(\frac{\partial n}{\partial t} + R \right) \\ \nabla \cdot J_p &= e \left(-\frac{\partial p}{\partial t} - R \right) \\ J_n &= e(D_n \nabla n - \mu_n n \nabla \phi) \\ J_p &= e(-D_p \nabla p - \mu_p p \nabla \phi) \end{aligned} \quad (8)$$

where ϕ denotes the electrical potential, n and p are the free carrier concentrations of electrons and holes, respectively, and J_n and J_p are the electron and hole current density, respectively. D_n , D_p , μ_n , and μ_p are the diffusion coefficients and the mobilities

of electrons and holes, respectively, and R is the recombination rate. The apparent capacitance is expressed as

$$C_{\text{app}} = -\frac{\text{Im}(\tilde{J})}{\omega \phi_{\text{ext}}} = -\frac{\text{Im}(J_n + J_p)}{\omega \phi_{\text{ext}}} \quad (9)$$

Minority carrier injection causes a current flow because majority carriers move to maintain charge neutrality. During minority carrier rearrangement in PVSK, a portion of the minority carriers diffuse to and exit via counter electrodes. Because this minority current is delayed in its arrival, the collection leads to a current that lags the applied voltage, resulting in an inductive effect, contributing negative components to the total diffusion capacitance (Figure 1c). Although there is no analytical solution for frequency dependence of the negative capacitance induced by bipolar injection, the numerical calculation yields a result very similar to Debye relaxation.^[42,43] There is another possible mechanism for negative capacitance. The negative capacitance in bipolar organic diodes is highly affected by trap-assisted recombination.^[44] These analyses exactly reproduce the small positive capacitance in the high-frequency range and the large negative capacitance in the middle-frequency range, which was observed in the present work. This result indicates that several components in Equation (7) are indeed induced by bipolar injection, not ionic-to-electronic current amplification.

The bipolar injection mechanism is supported by the impedance spectra for thick devices. The photoinduced capacitance for thin devices shows a distinctive frequency dependence; a small positive capacitance in the high-frequency range and

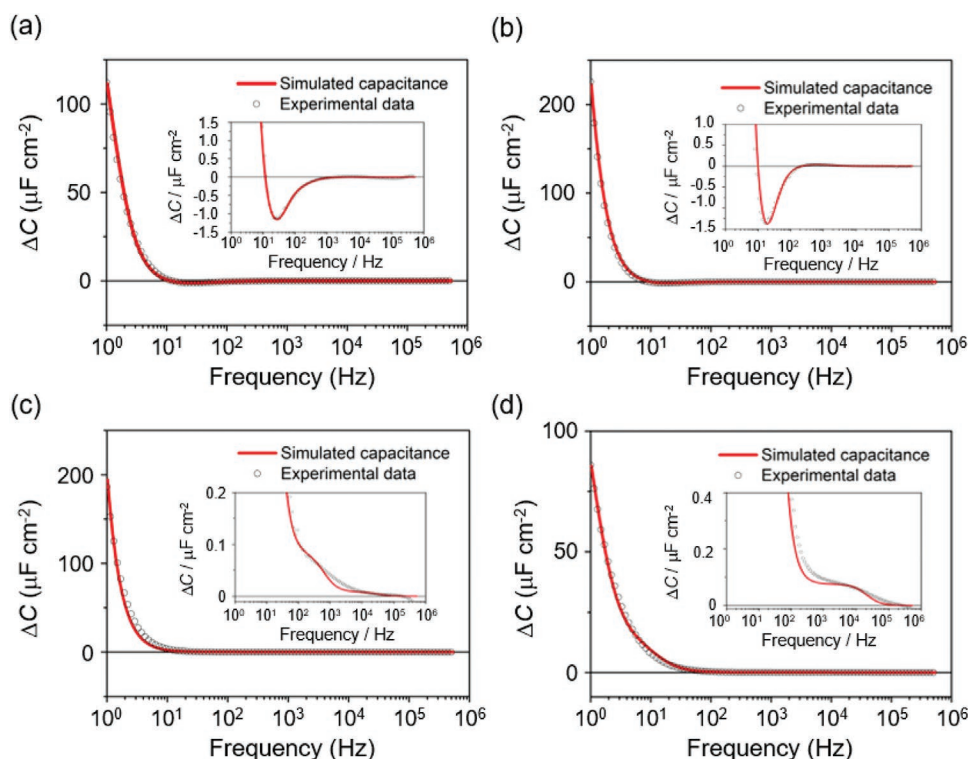


Figure 4. The photoinduced capacitance spectra measured under 0.4 sun for a) 30 nm, b) 150 nm, c) 350 nm, and d) 530 nm thick devices.

a large negative capacitance in the middle-frequency range (Figure 4a,b), whereas that for thick devices displays no negative capacitance (Figure 4c,d). Furthermore, for thick devices, the photoinduced capacitance in the middle- and high-frequency ranges cannot be fitted with the Debye relaxation (Figure 4c,d inset). Because the thin devices are “short” diodes, minority carriers can reach the counter electrode, resulting in the previously discussed negative capacitance. However, thick devices are “long” diode; thus, minority carriers undergo recombination before exit via the counter electrode. Therefore, no negative capacitance occurs in thick devices. The only question in the case of the bipolar injection model is why the negative capacitance is enhanced by light illumination. This enhancement might originate from the high conductivity of illuminated PVSK. The amount of injected minority carriers is highly modulated by the open-circuit voltage, which is determined by the illumination power. Therefore, the negative capacitance is substantially enlarged by illumination in PVSK solar cells.

To obtain further evidence, unipolar injection devices were fabricated to confirm the effect of bipolar injection. The negative capacitance disappeared from both *h*-only and *e*-only devices, as predicted by the bipolar injection model. Furthermore, as observed for the thick devices, the photoinduced capacitances in the middle- and high-frequency ranges cannot be fitted with Debye relaxation (Figure 5b,c). This result obviously indicates that the photoinduced capacitances in these frequency ranges are not induced by ionic-to-electronic current amplification. By contrast, the photoinduced capacitance in the low-frequency range is clearly fittable with Debye relaxation, implying that this one originates from the ionic-to-electronic current amplification. Furthermore,

the photoinduced capacitance in the low-frequency range shows a clear thickness dependence based on Equation (4) (Figure 2a) and nearly constant characteristic time, τ , for all of the devices (Tables S1 and S2, Supporting Information). All of these results strongly support that the hypothesis that ionic-to-electronic current amplification occurs in the low-frequency range.

In addition, capacitances of unipolar devices under dark conditions vary with the device structure, whereas the photoinduced capacitances show a very similar frequency dependence (Figure 5). In particular, the capacitance in the low-frequency range for *h*-only device becomes negative, implying that the capacitances of the PVSK solar cells are strongly affected by ionic-to-electronic current amplification even under dark conditions (Figure 5f). Impedance spectroscopy is widely used to analyze the trap distribution in PVSK solar cells.^[7–11] These analyses presuppose that the capacitance in the low-frequency range is only affected by the chemical capacitance of PVSK. However, impedance spectra for unipolar injection devices demonstrate that the capacitance of PVSK is obviously affected by the ionic-to-electronic current amplification. Thus, analysis of the trap distribution in PVSK solar cells by impedances spectroscopy should be performed with careful consideration of both the ionic-to-electronic current amplification and the bipolar injection model.

3. Conclusion

In summary, the photoinduced capacitances of PVSK solar cells were analyzed by impedance spectroscopy. The analysis clarifies

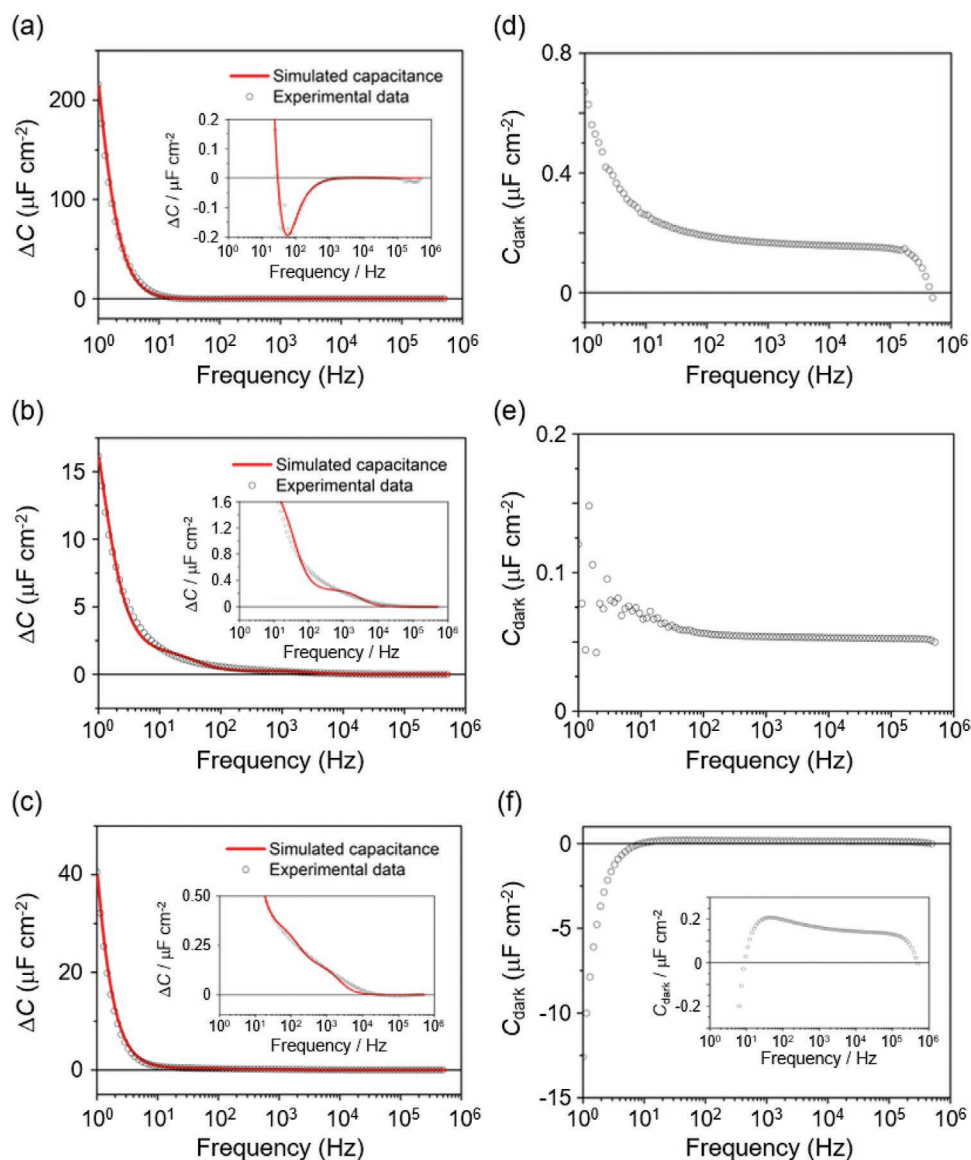


Figure 5. The photoinduced capacitance spectra measured under 0.4 sun for a) the normal perovskite device, b) the ϵ -only device, and c) the h -only device. The apparent capacitance measured in dark condition for d) the normal perovskite device, e) the ϵ -only device, and f) the h -only device.

that photoinduced capacitance involves several components with different characteristic time. The film thickness dependence of the photoinduced capacitance in the low-frequency range well matches the ionic-to-electronic current amplification model. Furthermore, the characteristic time for Debye relaxation in the low frequency range is independent of device structures as well as illumination powers. These results indicate that the photoinduced capacitance in the low-frequency range is determined by ionic-to-electronic current amplification. By contrast, the characteristic times of the photoinduced capacitances in the middle- and high-frequency ranges vary depending on the device configuration. The impedance spectra for unipolar injection devices demonstrate that the photoinduced capacitances in the middle- and high-frequency ranges originate from

bipolar injection. These results clearly indicate that the origin of the photoinduced capacitance in the low-frequency range differs from those in the middle- and high-frequency range.

4. Experimental Section

PVSK solar cell devices were fabricated in a planar heterojunction-type structure: indium tin oxide (ITO)/compact-SnO₂/perovskite/spiro-OMeTAD/Au. A 0.03 M SnCl₂ (Sigma-Aldrich) solution in ethanol was spin coated at 3000 rpm onto UV treated ITO substrates. Thereafter, thermal annealing was immediately performed at 150 °C for 30 min. A 0.03 M SnCl₂ (Sigma-Aldrich) solution in ethanol was again spin coated at 3000 rpm. The resulting film was annealed at 150 °C for 1 min and then transferred to a 180 °C oven for 1 h to form the compact-SnO₂

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layer. After UV treatment of the SnO_2 layer, perovskite layers were formed using solvent engineering and a typical spin-coating process. One millimole of $\text{Cs}_{0.05}\text{FA}_{0.95}\text{PbI}_3$ (Csl, Alfa Aesar; formamidinium iodide, Dyesol; PbI_2 , TCI) was dissolved in a mixed solvent of 1.0 mL of *N,N*-dimethylformamide (DMF) and 0.2 mL of *N*-methyl-2-pyrrolidone (NMP). Nonsolvent diethyl ether was dropped onto the center of the substrate as it was spun at 4000 rpm. Thermal annealing was immediately performed at 100 °C for 1 min to volatilize the NMP. The preannealed film was then transferred to a 150 °C oven to obtain cubic formamidinium perovskite. The thickness of the PVSK was varied by controlling the amount of DMF in the PVSK solution, and evaluated with stylus surface profiler (NanoMap-PS, AEP Technology) as well as atomic force microscope atomic force microscope (AFM) (MultiMode 8-HR AFM, Bruker). The PVSK solution for additive-free devices was prepared with FAPbI_3 by the same procedures. A solution for spiro layer was prepared by dissolving 74 mg of spiro-OMeTAD (Lumtec) in 1 mL of chlorobenzene. Then, 17.5 μL of LiTFSI (Sigma-Aldrich) solution (520 mg in 1 mL of acetonitrile (ACN)), 28.8 μL of tBP (4-*tert*-butylpyridine, Sigma-Aldrich), and 29 μL of tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine) cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK209, Sigma-Aldrich) (300 mg in 1 mL of ACN) were added to this solution. The solution for additive-free devices was prepared with only spiro-OMeTAD (i.e., without the chemical additives). The spiro layer was fabricated by spin-coating the solution at 2000 rpm. Finally, a 70 nm thick Au electrode was deposited as the top layer using thermal evaporation.

Unipolar injection devices were fabricated as follows. A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer was fabricated instead of compact- SnO_2 layer for *h*-only devices. PEDOT:PSS (Al 4083, Heraeus Clevios) solution was spin coated at 4000 rpm and then annealed at 120 °C for 40 min. The solution prepared by dissolving 10 μL of vanadium (V) oxytriisopropoxide (Sigma-Aldrich) in 3 mL of isopropanol was spin coated at 3000 rpm. Thereafter, thermal annealing was performed at 150 °C for 10 min. A phenyl-C61-butyric acid methyl ester (PCBM) layer was fabricated instead of spiro layer for *e*-only devices. The solution prepared by dissolving 20 mg of phenyl-C61-butyric acid methyl ester ([60]PCBM, Solenne BV) in 1 mL of chlorobenzene was spin coated at 2000 rpm. A 0.5 mg mL^{-1} solution of bathocuproine (Sigma-Aldrich) in ethanol was subsequently spin coated at 4000 rpm.

All of the impedance spectra were recorded with an impedance analyzer (MFIA, Zurich Instruments), without DC bias, under ≈ 1 sun light illumination provided by a Xe arc lamp.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

impedance spectroscopy, ionic to electronic response, negative capacitance, perovskite solar cells

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