Electrical properties of ion gels based on PVDF-HFP applicable as gate stacks for flexible devices

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ABSTRACT

Electrical characteristics of ion gels prepared by loading different amounts of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) in Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) are investigated and compared with those of ion liquid, [EMIM][TFSI] for possible application as a gate stack for flexible electronic devices. Capacitance and impedance as a function of frequency are measured, which can be well accounted for by a simple circuit model identifying the local device components. The operation of a flexible field effect transistor based on graphene and the ion gel as a top gate stack is also demonstrated.

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1. Introduction

To date, much research efforts have been directed toward the application of various new materials such as organic semiconductors, [1,2], carbon nanotubes, [3], graphene, [4], and two-dimensional (2D) transition dichalcogenide (TMD) [5] to electronic devices, especially flexible electronics utilizing the intrinsic flexibility of these materials. In such applications, the field effect transistor (FET) is regarded as a basic building block and usually the first device to demonstrate with any new electronic materials. The most common gate dielectric material for an FET is SiO_2 as many FETs based on the new materials are fabricated on a solid substrate such as the Si wafer. However, the efficiency of electric field gating depends on the thickness of SiO_2 and the rigid SiO_2 is not suitable for flexible applications. Therefore, apart from the active channel materials and electrodes, compatible gate dielectric materials are also required for the realization of the flexible electronic devices.

In recent years, ionic liquid (IL) [6–8] has attracted a great deal of interests as a gate dielectric for FETs based on organic materials [9] and 2D nanomaterials [10,11]. ILs can form an electric double layer (EDL) within the Debye length at the interface with these materials, which make it possible to induce large carrier density with small operating voltages [12]. Furthermore, ILs are thermally and chemically stable, nonvolatile, and have relatively large electrochemical windows, which also make them good material as a gate dielectric [6–8]. ILs can be made mechanically stable by forming an ion gel which is a mixture of IL and polymer. In an ion gel, the host polymer forms the structural backbones by networking while required electrical characteristics can be obtained by ILs filling the spaces in the polymer networks [13–17]. In this way, an ion gel is expected to be a good candidate for a gate dielectric for flexible FETs [18–20]. In most cases, there is a trade-off between the polymer contents in an ion gel and electrical characteristics such as capacitance, conductivity, and polarization time, which are related to the effectiveness of EDL formation and the device speed [21]. The more polymer contents in an ion gel, the better the mechanical integrity, while the more IL contents, the better desirable electrical characteristics as a gate dielectric are expected. Therefore, understanding the electrical properties of ion gels such as capacitance and impedance as a function of frequency and the IL content in an ion gel is a first step to assess the possibility of ion gels as gate stacks for flexible electron devices.

In this contribution, we investigated the electrical properties of an ion gel which is formed by loading 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) in Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-

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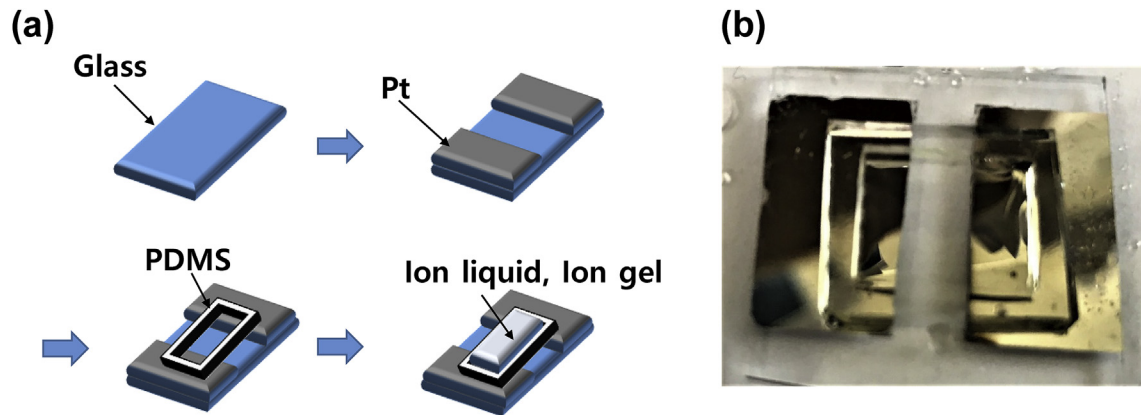
Fig. 1. (a) A fabrication schematic of planar electrodes for the impedance measurements. (b) A picture of the fabricated electrode with a PDMS well structure placed on.

HFP) as a gate stack for a flexible FET. We chose PVDF-HFP as a host polymer since it has good mechanical, thermal and chemical stabilities and is easy to form films with high tensile strength, which make it a good host material for an ion gel [13,22,23]. Most relevant electrical characteristics of the ion gel to the device operations such as capacitance and conductivity as a function of frequency are investigated depending on the relative IL contents in the ion gel in a planar electrode configuration. Finally, the operation of a flexible FET based on graphene and the ion gel as a gate stack is demonstrated.

2. Material and methods

2.1. Materials and preparation of ion gel

[EMIM][TFSI] is purchased from Merck and used as received. PVDF-HFP is purchased from Sigma-Aldrich. For the preparation of an ion gel, PVDF-HFP is first dissolved in acetone and the solution is mixed in a magnetic stirrer for 1 h. Then required amount of [EMIM][TFSI] is added to the solution and it is mixed in a magnetic stirrer for 1 day. Ion gel is formed on the target substrate by drop casting and letting solvent (acetone) evaporate (~10 min) in ambient conditions.

2.2. Electrode fabrication and impedance measurement

Fig. 1(a) shows the procedure for the fabrication of the electrodes for the impedance measurements. After a glass substrate is cleaned using acetone, IPA, and DI water, electrodes (20×10 mm^2 with a 5 mm-wide gap) were prepared by E-beam evaporation of 100 nm-thick Pt through a stencil mask for patterning. Then, a rectangular PDMS well is placed on the glass substrate covering both electrodes for the same area. Fig. 1(b) shows an example of the completed device. IL or ion gels is confined inside the PDMS well, ensuring the same area coverage. Impedance analyzer (CompactStat from IVIUM) was used for the measurement of capacitance and impedance, which were measured at room temperature and atmospheric pressure using 10 mV$_{rms}$ AC signal in the frequency range between 0.01 Hz and 100 kHz.

2.3. Graphene growth and transfer

Graphene was synthesized by low pressure chemical vapor deposition on a Cu foil (25 μm thick, from Alfa Aesar) as previously reported [24]. The Cu foil is first annealed at 1000 °C under H$_2$ flow (25 sccm) for 1 h. Then, graphene is grown for 10 min with the addition of CH$_4$ flow (2.5 sccm) at 1000 °C. Pressure is maintained at ~400 mTorr during the growth. After the growth, PMMA was spin-coated on the graphene/Cu foil and baked at 150 °C for 1 min. Oxygen plasma etching was used to remove the graphene on the back side of the Cu foil and the Cu foil is subsequently etched with Cu etchant. The remaining PMMA/Graphene film is transferred to a Si substrate with 300 nm-thick SiO$_2$, dried to get rid of moisture,
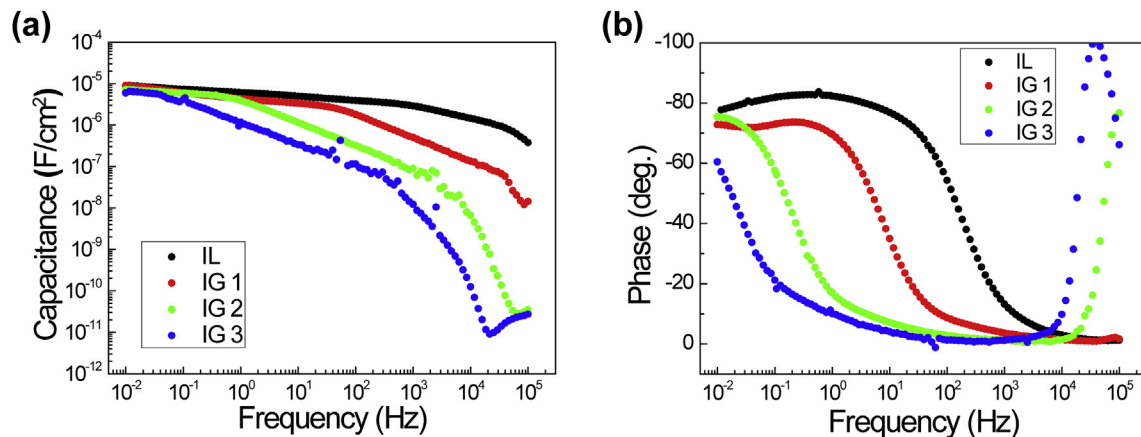
Fig. 2. (a) Capacitance as a function of frequency of ion gels with different IL:polymer weight ratio as marked in the legend and IL only. (b) Corresponding phases as a function of frequency.
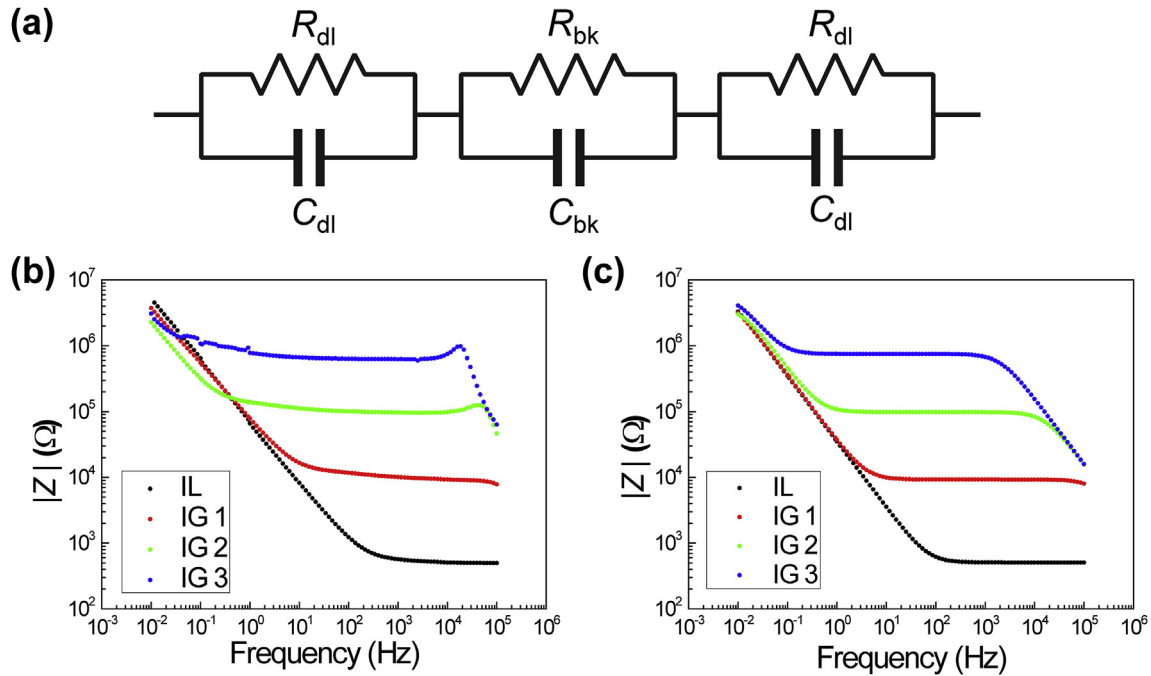
Fig. 3. (a) An equivalent circuit model for the samples. (b) Measured amplitude of impedance as a function of frequency between 0.01 Hz and 10^5 Hz. (c) Calculated amplitude of impedance using the equivalent circuit model in (a).

and PMMA is removed using acetone.

2.4. Flexible graphene FET fabrication and measurement

Electrode patterns are made on the transferred graphene on Si/SiO$_2$ using photolithography and e-beam evaporation (Ti 5 nm, Au 45 nm). Afterwards, graphene channel is formed by additional photolithography and etching with oxygen plasma. As-fabricated graphene devices with source, drain, and gate electrodes are transferred to a PET substrate as previously reported [25].

Briefly, after coating PMMA on the fabricated graphene FET devices on Si/SiO$_2$, SiO$_2$ layer is chemically etched with Buffered oxide etch. Then, floating PMMA/graphene FET film is rinsed in DI water and placed on a PET substrate. To remove moisture, it is annealed at 150 °C for 1 h and stored in a vacuum oven at 60 °C for 1 day. After drying, the PMMA was removed using acetone, which leaves only graphene devices on a PET substrate. The ion gel top gate is formed on the device by drop casting method. Bending of the device is achieved by putting the PET substrate between two slide glasses, one of which is moved by a translator. All the electrical measurements were carried out in the ambient conditions.

3. Results and discussions

Fig. 1 shows the electrode patterns we used for the measurements. Instead of typical sandwich configuration (thin ion gel films between the top and bottom electrodes), we employed planar electrode patterns as shown in Fig. 1 for the measurements. When an ion gel is used as a gate stack, it is typically used as a top gate. In this case, the electrical contact to the ion gel can be easily realized by a side electrode such as shown in Fig. 1(b), rather than a top electrode. Therefore, we employed the planar electrode pattern shown in Fig. 1(b) as it represents the actual device better although such configuration can make device slower since resistance of the ion gel becomes larger. We investigated ion gels with three different IL contents in polymer (IL: polymer weight ratio = 2:1, 1:1,
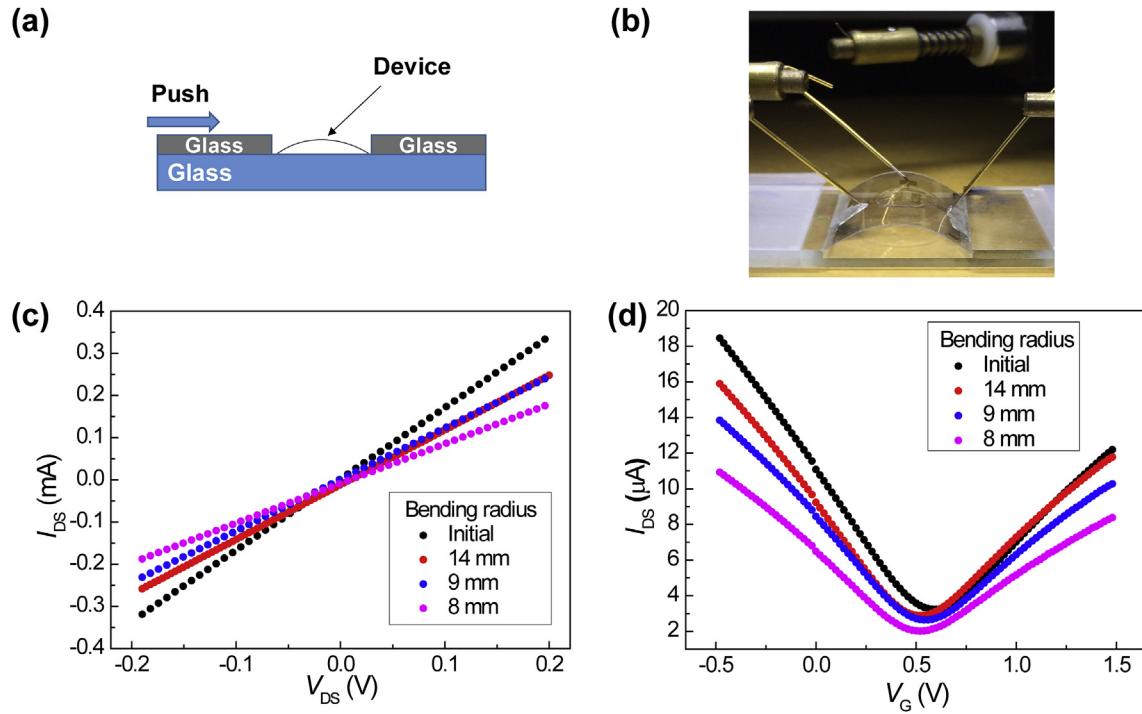
1:2, which will be referred as IG1, IG2, IG3 hereafter) and IL only.

Fig. 2 shows the measured capacitance and phase as a function of frequency of the ion gels and IL using the electrode patterns in Fig. 1(b). From the capacitance measurements in Fig. 2(a), two trends in capacitance can be observed. First, the low frequency capacitance values decrease as relative IL contents decrease. The low frequency capacitance of IL is ~9 μF/cm^2, similar to the reported values for [EMIM][TFSI] in the literature [26–28]. All the ion gels still show high capacitance values (6–9 μF/cm^2) comparable to that of IL at low frequency. The low frequency capacitance is due to the EDL formed at the interface between electrodes and IL. The ion gel with lowest IL in this measurement (IG3) shows reduced yet still high capacitance (~6 μF/cm^2). The decrease of capacitance with more polymer contents is expected since more area on the electrode is occupied by polymers. But the observed decrease is not significant such that all the ion gels investigated can still be expected to be utilized as a gate dielectric for the electrostatic doping. Second, the capacitance decreases with frequency and the decrease is more rapid for ion gels with less IL contents. Fig. 2(a) shows that the capacitance of IL decreases with frequency but is still higher than 1 μF/cm^2 up to ~25 kHz. However, the same frequency for 1 μF/cm^2 is 300 Hz, 10 Hz, and 1 Hz for IG1, IG2, and IG3, respectively. This frequency is related to the polarization time in the ion gels and the rapid decrease is due to the reduced conductivity of ion gels with the insulating polymer matrix. The frequency dependence determines the speed of a device when ion gel is used as a gate

Table 1
Summary of values for the circuit components in Fig. 3(a), obtained by fitting the experimental results in Fig. 3(b) with Eq. (1).

Device	C_{dl} (μF/cm^2)	R_{bk} (kΩ)	R_{dl} (MΩ)	C_{bk} (nF/cm^2)
IL	9.0	0.5	4.5	0.1
IG1	8.8	9.3	3.3	0.1
IG2	7.2	98	2.0	0.1
IG3	6.5	750	2.5	0.1

Fig. 4. (a) A schematic for the bending apparatus used. One glass is pushed or pulled by a linear translator. (b) A picture of the apparatus with a graphene FET and probes touched for the measurement. (c) I_{DS} vs V_{DS} (at $V_G = 0$ V) and (d) I_{DS} vs. V_G (at $V_{DS} = 10$ mV) for the specified bending radii.

dielectric. Fig. 2(b) shows the phase angles of the signal. For IL and ion gels (IG1, IG2), capacitive contribution dominates at low frequency (phase angle near $-90°$), while it becomes purely resistive (phase angle $\sim 0°$) at high frequency. Phase angle increases again at even higher frequency for some ion gels (IG2, IG3) due to the contribution of the bulk capacitance of the ion gel, rather than that of EDL at the interface. In case of IG3, the phase angle at low frequency is $\sim -60°$, showing that there is some resistive contribution even at the lowest frequency for this ion gel.

The impedances of the same samples are also measured and shown in Fig. 3(b). We propose that the electrodes-ion liquid/gel in Fig. 1(b) be represented by an equivalent circuit shown in Fig. 3(a). It can be divided into three parts, IL or ion gel itself and two interfaces between Pt electrodes and IL or ion gel. Each part is represented by a parallel connection of a resistor and a capacitor. R_{dl} and C_{dl} refer to the resistance and capacitance of the interface between electrode and IL or ion gel, respectively. It is assumed that both interfaces can be represented by the same R_{dl} and C_{dl} since electrodes are symmetric. R_{bk} and C_{bk} refer to the resistance and capacitance of IL or ion gel bulk, respectively. In this model, C_{dl} is the capacitance of the EDL and R_{dl} can be thought of as contact resistance at the metal electrode. Then, the magnitude of impedance Z can be calculated as,

dominates as represented by zero phase angle in Fig. 2(b). The bulk resistance increases with the polymer contents in the ion gel as expected (From 500 Ω for IL to ~ 1 MΩ for IG3). Then R_{dl}, which is the resistance of the contacts can be obtained from the low frequency impedance values (several MΩ for all the cases). At even higher frequencies, impedance decreases again due to the contribution of the bulk capacitance of the ion gel (C_{bk}). Table 1 summarizes the values of circuit components in Fig. 3(a), obtained as explained above. Fig. 3(c) is a plot of impedance according to Eq. (1) using the parameters in Table 1, which reproduces the measurement results in Fig. 3(b) quite well. This shows that simple circuit model in Fig. 3(a) is good for the ion gel/liquid-electrode system in Fig. 1(b). For the exact fitting of the results, we may need to include further circuit elements such as constant phase elements to incorporate the imperfect nature of the interfaces or the non-uniformity of the materials. However, the simple model in Fig. 3(a) is intuitive as it clearly identifies each local component in the system with the real physical meaning such as contact resistance (R_{dl}), EDL capacitance (C_{dl}), bulk resistance (R_{bk}) and bulk capacitance (C_{bk}). These measurements clearly show that all the ion gels investigated can form EDL at the interface, but with slower polarization times for ion gels with more polymer contents.

Therefore, we chose IG1, the ion gel with the largest IL content

$$|Z| = \sqrt{\left(\frac{2R_{dl}}{1+\omega^2 R_{dl}^2 C_{dl}^2} + \frac{R_{bk}}{1+\omega^2 R_{bk}^2 C_{bk}^2}\right)^2 + \left(\frac{2\omega C_{dl}R_{dl}^2}{1+\omega^2 R_{dl}^2 C_{dl}^2} + \frac{\omega C_{bk}R_{bk}^2}{1+\omega^2 R_{bk}^2 C_{bk}^2}\right)^2}. \tag{1}$$

C_{dl}, which corresponds to the EDL capacitance can be obtained from the low frequency capacitance values in Fig. 2(a). R_{bk}, which is the bulk resistance of IL or gel is obtained from the plateaued impedance values in the frequency range where the bulk resistance

for the application to the flexible graphene FET for its large EDL capacitance with the fast polarization time.

Fig. 4 shows the IV characteristics of a graphene FET on a flexible PET substrate with an ion gel (IG1) top gate. The device is

transferred to the PET substrate after fabricated on a Si/SiO_2 substrate as described in 2. Material and methods. Fig. 4(a) and (b) show the schematic for the bending apparatus and the actual measurement setup, respectively. Fig. 4(c) and (d) show the I_{DS}-V_{DS} and I_{DS}-V_G of the device with corresponding bending radii. Due to the large EDL capacitance of the ion gel, the graphene FET can be operated with on-off ratio larger than 5 in 2 V range as shown in Fig. 4(d). As the device is bent further (under more tensile strain), decrease of both the on- and off-state currents and the negative shift of Dirac point are observed. Graphene has been regarded as a good material for a flexible strain sensor as it shows a large gauge factor, is flexible and withstands large strain without failure [29–31]. The increase of overall resistance with tensile strain as observed in Fig. 4 is consistent with other reports of which origin is believed to be mostly piezoresistive [29,31,32]. Another possibility is that the contact between the metal electrode Au and the graphene is getting worse with strain, which can make the device more resistive as shown in Fig. 4(c). However, the deterioration of the contacts alone cannot account for the shift of Dirac points and increase of the off-state resistance observed in Fig. 4(d). Single layer graphene is also expected to develop bandgap under large uniaxial strain [33,34]. Although the strain applied in this report (0.7–1.5%) is not large enough to induce significant bandgap, the increased off-state resistance can be explained by the even small band gap opening due to the strain. Or it can be caused by the increase of carrier scattering due to the distortion in the graphene lattice under stain. Further careful measurement and analysis are required to elucidate the strain effect on the operation of graphene FETs with the ion gel gate stack.

4. Conclusions

In this study, we synthesized ion gels by mixing [EMIM][TFSI] and PVDF-HFP with different weight ratio, and measured their electrical properties such as capacitance and impedance at different frequency to access their applicability as a gate stack for flexible devices. Measured parameters are related to the device characteristics such as electrostatic doping efficiency and device speed. The capacitance of at low frequency which is the EDL capacitance remains high $(6-9 \mu F/cm^2)$ for all the ion gels and IL while it decreases rapidly with frequency for ion gels with less IL content. The electrical properties of ion gels and IL can be described by a simple circuit model of which each element can be associated with physical meaning such as contact or bulk resistance, and EDL or bulk capacitance. We also demonstrate the applicability of the ion gel as a gate stack by applying it as a top gate stack for a flexible graphene FET.

Acknowledgement

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